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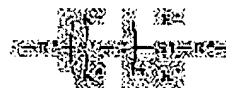
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(54) NONAQUEOUS SOLVENT BINDER COMPOSITION, METHOD OF MANUFACTURING ELECTRODE, ELECTRODE AND NONAQUEOUS SOLVENT SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain high adhesion property, high flexibility, and high electrolyte resistance by dissolving or dispersing siloxane modified polyamide-imide resin in a nonaqueous solvent.

SOLUTION: The siloxane modified polyamide-imide resin to be dissolved or dispersed in the nonaqueous solvent is preferably obtained by the reaction of a mixture of siloxane diamine and aromatic diamine or aliphatic diamine with multivalent carboxylic acid or di-isocyanate, or preferably obtained by the reaction of a reaction product represented by formula I of di-imide dicarboxylic acid obtained by the reaction of a mixture of siloxane diamine and aromatic diamine or aliphatic diamine with trimellitic anhydride, with di-isocyanate. In formula I, R1 is a group represented by formula II; R2 and R3 are each divalent organic group; R4-R7 are each 1-12C alkyl group or a 6-18C aryl group; and n is an integer of 1-50. A



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nonaqueous solvent binder composition obtained is useful for an electrode for a nonaqueous solvent secondary battery.

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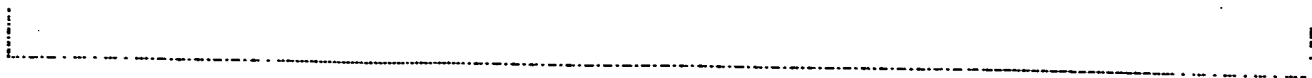
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(54) 【発明の名称】 非水溶媒系バインダ組成物、電極の製造法、電極及び非水溶媒系二次電池

(57) 【要約】

【課題】 接着性、屈曲性及び耐電解液性が優れ、非水溶媒系二次電池の電極に極めて有用な非水溶媒系バインダ組成物、接着性、屈曲性、耐電解液性、電池にしたときのサイクル寿命特性及び高温下での接着性が優れ、非水溶媒系二次電池に極めて有用な電極の製造法、接着性、屈曲性、耐電解液性、電池にしたときのサイクル寿命特性及び高温下での接着性が優れ、活物質の増量に有効で体積エネルギー密度を増大することができる電極並びにサイクル寿命特性、耐電解液性及び高温下での接着性が優れ、活物質の増量に有効で体積エネルギー密度を増大することができ、破裂・爆発危険性が小さく、安全性が高い非水溶媒系二次電池の製造法を提供する。

【解決手段】 (A) シロキサン変性ポリアミドイミド樹脂を非水溶媒に溶解又は分散させた非水溶媒系バインダ組成物、この非水溶媒系バインダ組成物と活物質とを混合し、電極基材表面に塗布後、非水溶媒を除去することを特徴とする電極の製造法、この電極の製造法により製造された電極並びに非水溶媒系二次電池の少なくとも一方の極に前記電極を用いた非水溶媒系二次電池。



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【特許請求の範囲】

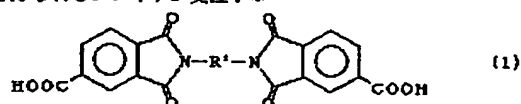
【請求項1】 (A) シロキサン変性ポリアミドイミド樹脂を非水溶媒に溶解又は分散させた非水溶媒系バインダ組成物。

【請求項2】 (A) 成分のシロキサン変性ポリアミドイミド樹脂が、シロキサジアミンと芳香族ジアミン又は脂肪族ジアミンとの混合物と多価カルボン酸又はジイソシアネートとを反応させて得られるシロキサン変性ポ*

*リアミドイミド樹脂である請求項1記載の非水溶媒系バインダ組成物。

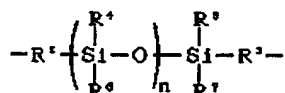
【請求項3】 (A) 成分のシロキサン変性ポリアミドイミド樹脂が、シロキサジアミンと芳香族ジアミン又は脂肪族ジアミンとの混合物と無水トリメリット酸とを反応させて得られる一般式(1)

【化1】



【式中、R'は

【化2】



(式中、R'及びR'は各々独立に2価の有機基を示し、R', R', R'及びR'は各々独立に炭素数1~20のアルキル基、炭素数6~18のアリール基を示し、nは1~50の整数である)で示されるジイミドジカルボン酸を含有する反応物にジイソシアネートを反応させて得られるシロキサン変性ポリアミドイミド樹脂である請求項1又は2記載の非水溶媒系バインダ組成物。

【請求項4】 さらに(B)熱硬化性樹脂を非水溶媒に溶解又は分散させた請求項1、2又は3記載の非水溶媒系バインダ組成物。

【請求項5】 (B)成分の熱硬化性樹脂が、2個以上のグリシジル基を有するエポキシ樹脂である請求項4記載の非水溶媒系バインダ組成物。

【請求項6】 請求項1、2、3、4又は5記載の非水溶媒系バインダ組成物と活物質とを混合し、電極基体表面に塗布後、非水溶媒を除去することを特徴とする電極の製造法。

【請求項7】 活物質が、充放電により可逆的にリチウムイオンを挿入又は放出できる遷移金属酸化物である請求項6記載の電極の製造法。

【請求項8】 遷移金属酸化物が一般式 $L_xM_nO_y$ (xは0.2≤x≤2.5の範囲であり、yは0.8≤y≤1.25の範囲である)で示されるリチウムマンガニ複合酸化物である請求項7記載の電極の製造法。

【請求項9】 請求項6、7又は8記載の電極の製造法により製造された電極。

【請求項10】 非水溶媒系二次電池の少なくとも一方の極に請求項9記載の電極を用いた非水溶媒系二次電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、非水溶媒系バイン

ダ組成物、電極の製造法、電極及び非水溶媒系二次電池に関する。

【0002】

【従来の技術】電子技術の進歩により、電子機器の性能が向上し、小型、ポータブル化が進み、電源として高エネルギー密度の電池が望まれている。従来の二次電池として、鉛蓄電池、ニッケル、カドミウム電池が挙げられるが、エネルギー密度の高い電池を得るという点では未だ不十分である。そこで、これらの電池に替わるものとして、高エネルギー密度の有機電解液二次電池(以下リチウム二次電池と記す)が開発され、急速に普及している。

【0003】リチウム二次電池は、正極にリチウムコバルト複合酸化物等のリチウム複合金属酸化物を、負極にはリチウムを吸蔵放出可能で優れた可とう性やリチウムの析出の恐れが少ない炭素材料が用いられ、これらとバインダ樹脂とをN-メチル-2-ピロリドン(NMP)に分散させてスラリーとしたものを集電体である金属箔上に両面塗布し、溶剤を乾燥した後、ローラープレス機にて圧縮成形して正・負極板を得ている。バインダとして主にポリフッ化ビニリデン(PVDF)が多く使用されている。

【0004】しかしながら、ポリフッ化ビニリデンをバインダとして使用した場合、集電体と合剤層との界面の密着及び合剤層相互間の密着性が劣るため、極板の截断工程や捲回工程等の製造工程時に合剤の一部が集電体から剥離・脱落して減少短絡や電池容量ばらつきの原因となる。また、充放電を繰り返すことによって特に負極の炭素材料は膨張・収縮するため、合剤が集電体から剥離・脱落したり、合剤相互間の密着の低下により、集電効率の低下、リチウムとの反応の不均一が生じて電池容量が次第に低下するという問題があった。

【0005】さらに特開平6-172452号公報に記載のフッ化ビニリデンを主成分とする単量体と不飽和二塩基性モノエステルとを共重合して得られたフッ化ビニリデン系共重合体をバインダとする場合、集電体との密着強度は向上するものの、高電圧下での異常温度上昇により分解してフッ化水素が発生し、負極板表面のリチウ

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ム層間化合物(GIC)や析出した金属リチウムと反応して異常発熱して、電池が破裂・爆発する恐れがあった。

【0006】ポリフッ化ビニリデン等のフッ素樹脂以外のバインダとして、例えば特開平5-74461号公報に記載のステレンブタジエンゴム(SBR)系合成ゴム、特開平9-87571号公報に記載のジエン系ゴムを含む合成ゴムや特開平6-163031号公報に記載のポリイミド樹脂等の熱可塑性樹脂を使用する提案がなされている。しかし、これらは電解液に対して溶解もしくは大きく膨潤して、集電体と合剤層との界面の密着及び合剤層相互間の密着性を長期間維持できない。また、ポリイミド樹脂を用いる場合、合剤層を形成しても可とう性が低く、作製した電極を捲回する際に合剤層の割れ、剥離が生じて容量を低下させる。ステレンブタジエンゴム等のジエン系合成ゴムは耐電解液性を有するものの活物質とバインダ等との均一分散が非常に困難であり、セルロースや界面活性剤等の添加が必要で、これらが電解液に溶解して電池の充放電効率を低下させる。

【0007】

【発明が解決しようとする課題】請求項1記載の発明は、接着性、屈曲性及び耐電解液性が優れ、非水溶媒系二次電池の電極に極めて有用な非水溶媒系バインダ組成物を提供するものである。請求項2記載の発明は、請求項1記載の発明の効果に加えて、さらに接着性及び耐熱性が優れ、非水溶媒系二次電池の電極に極めて有用な非水溶媒系バインダ組成物を提供するものである。請求項3記載の発明は、請求項1又は2記載の発明の効果を奏し、さらに耐熱性が優れ、非水溶媒系二次電池の電極に極めて有用な非水溶媒系バインダ組成物を提供するものである。

【0008】請求項4記載の発明は、請求項1、2又は3記載の発明の効果を奏し、さらに耐熱性及び耐電解液性が優れ、非水溶媒系二次電池の電極に極めて有用な非水溶媒系バインダ組成物を提供するものである。請求項5記載の発明は、請求項4記載の発明の効果を奏し、さらに耐熱性及び耐電解液性が優れ、非水溶媒系二次電池*

*の電極に極めて有用な非水溶媒系バインダ組成物を提供するものである。請求項6記載の発明は、接着性、屈曲性、耐電解液性、電池にしたときのサイクル寿命特性及び高温下での接着性が優れ、非水溶媒系二次電池に極めて有用な電極の製造法を提供するものである。

【0009】請求項7記載の発明は、請求項6記載の発明の効果を奏し、さらに電池にしたときのサイクル寿命特性が優れ、非水溶媒系二次電池に極めて有用な電極の製造法を提供するものである。請求項8記載の発明は、請求項7記載の発明の効果を奏し、さらに電池にしたときのサイクル寿命特性が優れ、非水溶媒系二次電池に極めて有用な電極の製造法を提供するものである。

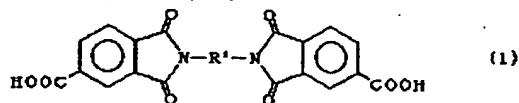
【0010】請求項9記載の発明は、接着性、屈曲性、耐電解液性、電池にしたときのサイクル寿命特性及び高温下での接着性が優れ、活物質の増量に有効な体積エネルギー密度を増大することができる電極を提供する。請求項10記載の発明は、サイクル寿命特性、耐電解液性及び高温下での接着性が優れ、活物質の増量に有効な体積エネルギー密度を増大することができ、破裂・爆発危険性が小さく、安全性が高い非水溶媒系二次電池の製造法を提供する。

【0011】

【課題を解決するための手段】本発明は、(A)シロキサン変性ポリアミドイミド樹脂を非水溶媒に溶解又は分散させた非水溶媒系バインダ組成物に関する。また、本発明は、(A)成分のシロキサン変性ポリアミドイミド樹脂が、シロキサジアミンと芳香族ジアミン又は脂肪族ジアミンとの混合物と多価カルボン酸又はジイソシアネートとを反応させて得られるシロキサン変性ポリアミドイミド樹脂である前記非水溶媒系バインダ組成物に関する。

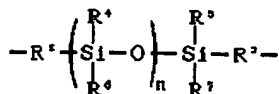
【0012】また、本発明は、(A)成分のシロキサン変性ポリアミドイミド樹脂が、シロキサジアミンと芳香族ジアミン又は脂肪族ジアミンとの混合物と無水トリメリット酸とを反応させて得られる一般式(1)

【化3】



【式中、R¹は

【化4】



(式中、R²及びR³は各々独立に2価の有機基を示し、R²、R³、R⁴及びR⁵は各々独立に炭素数1~20のアルキル基、炭素数6~18のアリール基を示し、nは1

~50の整数である)である]で示されるジイミドジカルボン酸を含有する反応物にジイソシアネートを反応させて得られるシロキサン変性ポリアミドイミド樹脂である前記非水溶媒系バインダ組成物に関する。

【0013】また、本発明は、さらに(B)熱硬化性樹脂を非水溶媒に溶解又は分散させた前記非水溶媒系バインダ組成物に関する。また、本発明は、(B)成分の熱硬化性樹脂が、2個以上のグリシジル基を有するエポキシ樹脂である前記非水溶媒系バインダ組成物に関する。

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また、本発明は、前記非水溶媒系バインダ組成物と活物質とを混合し、電極基体表面に塗布後、非水溶媒を除去することを特徴とする電極の製造法に関する。

【0014】また、本発明は、活物質が、充放電により可逆的にリチウムイオンを挿入又は放出できる遷移金属酸化物である前記電極の製造法に関する。また、本発明は、遷移金属酸化物が一般式 $L_xMn_yO_z$ (x は0.2 $\leq x \leq 2.5$ の範囲であり、 y は0.8 $\leq y \leq 1.2$ の範囲である)で示されるリチウムマンガン複合酸化物である前記電極の製造法に関する。

【0015】また、本発明は、前記電極の製造法により製造された電極に関する。また、本発明は、非水溶媒系二次電池の少なくとも一方の極に前記電極を用いた非水溶媒系二次電池に関する。

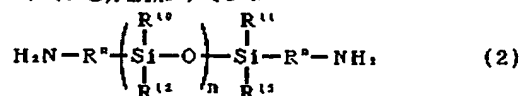
【0016】

【発明の実施の形態】本発明の非水溶媒系バインダ組成物は(A)シロキサン変性ポリアミドイミド樹脂を非水溶媒に溶解又は分散させる必要がある。

【0017】上記(A)シロキサン変性ポリアミドイミド樹脂は、例えば、①シロキサンジアミンと②芳香族ジアミン又は脂肪族ジアミンの混合物(①/②=50/50~100/0モル比)の合計モル数と多価カルボン酸又はジイソシアネートのモル比が1/2.20~1/2.05で反応させて得ることができる。上記①/②のモル比は50/50~100/0であることが好ましく、70/30~100/0であることがより好ましい。このモル比が50/50未満では接着性が低下する傾向がある。

【0018】前記①シロキサンジアミンと②芳香族ジアミン又は脂肪族ジアミンの混合物の合計モル数と多価カルボン酸又はジイソシアネートのモル比は1/2.20~1/2.05であることが好ましく、1/2.15~1/2.10であることがより好ましい。このモル比が1/2.20未満では接着性が低下する傾向があり、1/2.05を超えると耐熱性が低下する傾向がある。

【0019】また、前記(A)シロキサン変性ポリアミドイミド樹脂は、シロキサンジアミンと芳香族ジアミン*



(式中、 R^a 及び R^b は各々独立に2価の有機基を示し、 R^{10} 、 R^{11} 、 R^{12} 及び R^{13} は各々独立に炭素数1~20のアルキル基、炭素数6~18のアリール基を示し、 n は1~50の整数である)で表されるものが用いられ

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*又は脂肪族ジアミンとの混合物と無水トリメリット酸とを反応させて得られる一般式(1)で示されるジイミドジカルボン酸を含有する反応物にジイソシアネートを反応させて得られるシロキサン変性ポリアミドイミド樹脂であることが好ましい。

【0020】前記一般式(1)中、2価の有機基としては、例えば、メチレン基、エチレン基、プロピレン基等のアルキレン基、フェニレン基、トリレン基、キシリレン基等のアリーレン基などが挙げられる。前記一般式

(1)中、炭素数1~20のアルキル基としては、例えば、メチル基、エチル基、 n -プロピル基、イソプロピル基、 n -ブチル基、イソブチル基、sec-ブチル基、tert-ブチル基、ペンチル基、イソペンチル基、ネオペンチル基、ヘキシル基、ヘプチル基、オクチル基、ノニル基、デシル基、ウンデシル基、ドデシル基、トリデシル基、テトラデシル基、ペンタデシル基、ヘキサデシル基、ヘプタデシル基、オクタデシル基、ノナデシル基、イコシル基、これらの構造異性体等が挙げられる。前記一般式(1)中、炭素数6~18のアリール基としては、例えば、フェニル基、トリル基、キシリル基、ビフェニル基、ナフチル基、アントリル基、フェナントリル基等が挙げられ、ハロゲン原子、アミノ基、ニトロ基、シアノ基、メルカプト基、アリル基、炭素数1~20のアルキル基等で置換されていてもよい。

【0021】前記一般式(1)で示されるジイミドジカルボン酸を得るためのシロキサンジアミンと無水トリメリット酸とのモル比は1/2.20~1/2.05であることが好ましく、1/2.15~1/2.10であることがより好ましい。次いで前記一般式(1)で示されるジイミドジカルボン酸とジイソシアネートをモル比1/1.50~1/1.05で反応させてことが好ましく、1/1.35~1/1.20で反応させることがより好ましい。

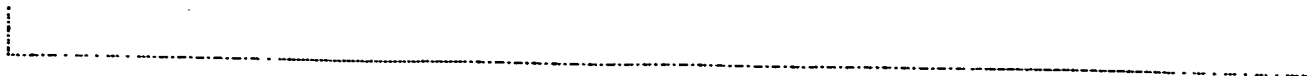
【0022】前記シロキサンジアミンとしては、例えば、一般式(2)

【化5】

る。

【0023】このようなシロキサンジアミンとしては下記式

【化6】

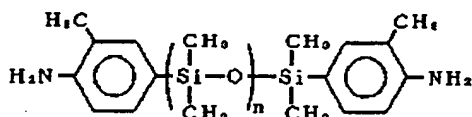
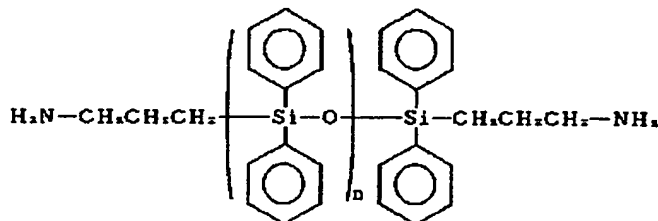
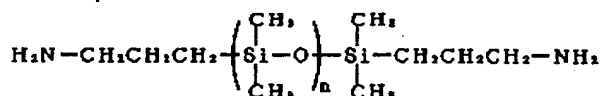


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(式中、nは1～50の整数である)に示すもの等が挙げられる。

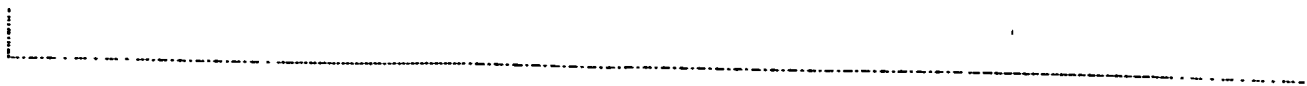
【0024】商業的に入手可能なものとしては、例えば、これらの中でもシロキサン系両末端アミンであるアミノ変性シリコンオイルX-22-161A(アミン当量450、信越化学工業(株)製商品名)、X-22-161A(アミン当量840、信越化学工業(株)製商品名)、X-22-161B(アミン当量1500、信越化学工業(株)製商品名)、BY16-853(アミン当量650、東レダウコーニングシリコン(株)製商品名)、BY16-853B(アミン当量2200、東レダウコーニングシリコン(株)製商品名)等が挙げられる。シロキサンジアミンは、接着性、屈曲性の点からジアミン中50モル%以上用いることが好ましい。これらは単独で又は2種類以上を組み合わせて使用される。

【0025】前記芳香族ジアミンとしては、例えば、o-フェニレンジアミン、m-フェニレンジアミン、p-フェニレンジアミン、3,3'-ジアミノジフェニルエーテル、4,4'-ジアミノジフェニルエーテル、3,4'-ジアミノジフェニルエーテル、3,3'-ジアミノジフェニルジフルオロメタン、4,4'-ジアミノジフェニルジフルオロメタン、3,3'-ジアミノジフェニルスルホン、3,4'-ジアミノジフェニルスルホン、4,4'-ジアミノジフェニルスルホン、3,3'-ジアミノジフェニルスルフィド、3,4'-ジアミノジフェニルスルフィド、4,4'-ジアミノジフェニルケトン、3,4'-ジアミノジフェニルケトン、2,2-ビス(3-アミノフェニル)プロパン、2,2-(3,4'-ジアミノジフェニル)プロパン、2,2-(3,4'-ジアミノジフェニル)ヘキサフルオロプロパン、2,2-ビス(4-アミノフェニル)ヘキサフルオロプロパン、1,3-ビス

(3-アミノフェノキシ)ベンゼン1,4-ビス(4-アミノフェノキシ)ベンゼン、3,3'-[1,4-フェニレンビス(1-メチルエチリデン)]ビスアニリン、3,4'-[1,4-フェニレンビス(1-メチルエチリデン)]ビスアニリン、4,4'-[1,4-フェニレンビス(1-メチルエチリデン)]ビスアニリン、2,2-ビス[4-(3-アミノフェノキシ)フェニル]プロパン、2,2-ビス[4-(4-アミノフェノキシ)フェニル]プロパン、2,2-ビス[4-(3-アミノフェノキシ)フェニル]ヘキサフルオロプロパン、2,2-ビス[4-(4-アミノフェノキシ)フェニル]ヘキサフルオロプロパン、ビス[4-(3-アミノフェノキシ)フェニル]スルフィド、ビス[4-(3-アミノフェノキシ)フェニル]スルホン、ビス[4-(4-アミノフェノキシ)フェニル]スルホン等が挙げられる。これらの中でも芳香族環を3個以上有するものであることが好ましい。これらは単独で又は2種類以上を組み合わせて使用される。

【0026】前記脂肪族ジアミンとしては、例えば、アルキレンジアミン、ポリオキシアルキレンジアミン等がある。また、イソホロンジアミン、4,4'-ジシクロヘキシルメタンジアミン等の脂環式ジアミン、3,9-ビス(3-アミノプロピル)-2,4,8,10-テトラスピロ[5.5]ウンデカン等の複素環式ジアミンなどが挙げられる。これらは単独で又は2種類以上を組み合わせて使用される。芳香族ジアミンと脂肪族ジアミンの比は、芳香族ジアミン/脂肪族ジアミンの合計量に対し、耐熱性の点から20重量%以下で用いることが好ましい。

【0027】前記多価カルボン酸としては、例えば、シュウ酸、マロン酸、コハク酸、グルタル酸、アジピン酸、ピメリン酸、アゼライン酸、セバシン酸、ドデカン二酸、エイコサン二酸等のアルキレンテール結合含有



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ジカルボン酸、アルキレンカーボネート結合含有ジカルボン酸、フタジエン結合含有ジカルボン酸等の脂肪族ジカルボン酸、フタル酸、イソフタル酸、テレフタル酸、ナフタレンジカルボン酸等の芳香族ジカルボン酸、ブタン-1, 2, 4-トリカルボン酸、ナフタレン-1, 2, 4-トリカルボン酸、トリメリット酸等のトリカルボン酸、ブタン-1, 2, 3, 4-テトラカルボン酸、ピロメリット酸、ベンゾフェノン-3, 3', 4, 4'-テトラカルボン酸、ジフェニルエーテル-3, 3', 4, 4'-テトラカルボン酸等のトリカルボン酸、ビフェニル-3, 3', 4, 4'-テトラカルボン酸、ナフタレン-2, 3, 6, 7-テトラカルボン酸、ナフタレン-1, 2, 4, 5-テトラカルボン酸、ナフタレン-1, 2, 5, 8-テトラカルボン酸等のカルボン酸、無水トリメット酸などが挙げられる。脂肪族ジカルボン酸は、耐熱性の点から多価カルボン酸中の20モル%以下で用いることが好ましい。これらは単独で又は2種類以上を組み合わせて使用される。

【0028】前記芳香族ジイソシアネートとしては、例えば、4, 4'-ジフェニルメタンジイソシアネート（以下、MDIと略す）、2, 4-トリレンジイソシアネート、2, 6-トリレンジイソシアネート、1, 5-ナフタレンジイソシアネート、トリレンジイソシアネート、p-フェニルジイソシアネート、4, 4'-ジフェニルエーテルジイソシアネート、m-キシリレンジイソシアネート、m-テトラメチルキシリレンジイソシアネート等の芳香族ジイソシアネート、1, 6-ヘキサメチレンジイソシアネート、2, 2, 4-トリメチルヘキサメチレンジイソシアネート、2, 4, 4-トリメチルヘキサメチレンジイソシアネート等の脂肪族ジイソシアネート、イソホロンジイソシアネート、4, 4'-ジシクロヘキシルメタンジイソシアネート等の脂環式ジイソシアネートなどが挙げられる。脂肪族ジイソシアネートは、耐熱性の点から10モル%以下で用いることが好ましい。これらは単独で又は2種類以上を組み合わせて使用される。

【0029】本発明で用いる(A)成分のシロキサン変性ポリアミドイミド樹脂は、例えば、芳香族ジアミン又は脂肪族ジアミン(I)及びシロキサンジアミン(II)の混合物((I)/(II)=0.1/99.9~99.9/0.1モル比)と無水トリメリット酸（以下、TMAと略す）を((I)+(II)の合計モル数とTMAのモル比が1/2.20~1/2.05で非プロトン性極性溶媒の存在下に、50~90℃程度で0.2~1.5時間程度反応させ、さらに水と共沸可能な芳香族炭化水素を非プロトン性極性溶媒の0.1~0.5重量%程度で投入し、120~180℃で反応を行い、シロキサンジイミドジカルボン酸を含む混合物を製造し、これと芳香族ジイソシアネート(III)とを150~250℃程度で0.5~3時間程度反応((I)+(II)/(III)=1 50

/1.50~1/1.05モル比)を行うことで製造できる。また、芳香族ジイミドジカルボン酸を製造した後、その溶液を150~250℃程度にすることでその溶液から芳香族炭化水素を除去し、これと芳香族ジイソシアネートとの反応を行うことによって製造することもできる。また、シロキサン変性ポリアミドイミド樹脂は非プロトン性極性溶媒を含むワニスであることが好ましい。

【0030】前記非プロトン性極性溶媒としては、シロキサンジアミン及びTMAと反応しない有機溶媒であることが好ましく、例えば、ジメチルアセトアミド、ジメチルホルムアミド、ジメチルスルホキシド、N-メチル-2-ピロリドン、γ-ブチロラクトン、スルホラン、シクロヘキサノン等が挙げられ、イミド化反応には、高温を要するため沸点の高い、N-メチル-2-ピロリドンが特に好ましい。上記非プロトン性極性溶媒中に含まれる水分量はTMAが水和して生成するトリメリット酸により、十分に反応が進行せず、ポリマーの分子量低下の原因になるため、0.2重量%以下で管理されていることが好ましい。また、本発明で使用する非プロトン性極性溶媒は、特に制限されないが、シロキサンジアミン及びTMAを合わせた重量の割合が多いとTMAの溶解性が低下し十分な反応が行えなくなることや、逆に低いと工業的製造法として不利であることから、10~70重量%の範囲になることが好ましい。これらは単独で又は2種類以上を組み合わせて使用される。

【0031】本発明の(A)シロキサン変性ポリアミドイミド樹脂の重量平均分子量は、特性のバランスから30,000~100,000であることが好ましく、45,000~85,000であることがより好ましい。この重量平均分子量が30,000未満では耐熱性が低下する傾向があり、100,000を超えると接着性が低下する傾向がある。本発明において、重量平均分子量は、ゲルパーミエーションクロマトグラフィー法(GPC)により標準ポリスチレンによる換算値を用いて測定される。

【0032】本発明の非水溶媒系バインダ組成物には必要に応じて、(B)熱硬化性樹脂を含有させることができる。上記熱硬化性樹脂としては、例えば、エポキシ樹脂、フェノール樹脂、ポリエステル樹脂、ポリイミド樹脂、ビスマレイミドトリアジン樹脂等が挙げられる。

【0033】接着性、取り扱い性の点からはエポキシ樹脂が特に好ましく、上記エポキシ樹脂としては、例えば、ビスフェノールA型エポキシ樹脂、ビスフェノールF型エポキシ樹脂、ビスフェノールS型エポキシ樹脂、フェノールノボラック型エポキシ樹脂、クレゾールノボラック型エポキシ樹脂、ナフタレン型エポキシ樹脂及びその変性物、ヒキシレンジグリシジルエーテル、YDC1312（東都化成製）、TMH574（住友化学製）、エピコート1031S（油化シェル製）、エボト

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ート8125（東都化成(株)製商品名）等の芳香族系エポキシ樹脂、ネオペンチルグリコールジグリシジルエーテル、ポリプロピレングリコールジグリシジルエーテル、テトラヒドロフタル酸ジグリシジルエステル等の脂肪族系エポキシ樹脂、トリグリシジルイソシアネート等の複素環式エポキシ化合物、エポリドPB3600（ダイセル化学(株)製商品名）などが挙げられる。

【0034】これらの中では2個以上のグリシジル基を有するエポキシ樹脂とその硬化促進剤を用いる事が好ましい。またグリシジル基は多いほど良く、3個以上であればさらに好ましい。グリシジル基の数により、配合量が異なり、グリシジル基が多い程、シリコーン変性ポリアミドイミド樹脂に対する配合量が少なくても良い。また、エポキシ樹脂の硬化剤を併用すればさらに好ましい。これらは単独で又は2種類以上を組み合わせて使用される。

【0035】本発明で用いるエポキシ樹脂の配合量は、接着性、屈曲性及び耐熱性の点から、(A)成分100重量部に対して5～100重量部であることが好ましく、10～50重量部であることがより好ましい。この配合量が5重量部未満では十分な耐電解液性が得られない傾向があり、100重量部を越えると十分な接着性及び屈曲性が得られない傾向がある。

【0036】前記エポキシ樹脂の硬化剤又は硬化促進剤としては、エポキシ樹脂と反応するもの、または、硬化を促進させるものであればどのようなものでもよく、例えば、アミン類、イミダゾール類、多官能フェノール類、酸無水物類等が挙げられる。上記アミン類としては、例えば、ジシアンジアミド、ジアミノジフェニルメタン、グアニル尿素等が挙げられる。上記イミダゾール類としては、例えば、2-エチル-4-メチルイミダゾール等のアルキル基置換イミダゾール、ベンゾイミダゾールなどが挙げられる。上記多官能フェノール類としては、例えば、ヒドロキノン、レゾルシノール、ビスフェノールA及びこれらのハロゲン化合物、前記多官能フェノール類とホルムアルデヒドとの付加縮合物であるノボラックフェノール型フェノール樹脂、レゾール型フェノール樹脂等が挙げられる。上記酸無水物類としては、例えば、無水フタル酸、ベンゾフェノンテトラカルボン酸二水和物、メチルハイミック酸等が挙げられる。このうち、硬化促進剤としては、イミダゾール類を用いることが特に好ましい。

【0037】これらの硬化剤または硬化促進剤の必要量は、アミン類の場合はアミンの活性水素の当量とエポキシ樹脂のエポキシ当量がほぼ等しくなる量が好ましい。イミダゾール類の場合は、単純に活性水素との当量比とならず、経験的にエポキシ樹脂100重量部に対して、0.1～10.0重量部必要となる。多官能フェノール類の場合、エポキシ樹脂のエポキシ基1当量に対して、0.6～1.2水酸基当量が必要である。これらの硬化

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剤または硬化促進剤の量は、少なければ未硬化のエポキシ樹脂が残存するため接着性が低下し、多すぎると未反応の硬化剤及び硬化促進剤が残存するため、耐電解液性が低下する。これらは単独で又は2種類以上を組み合わせて使用される。

【0038】本発明では、これらの組成物を固形分が10～30重量%程度になるように非水溶媒に溶解又は分散させて、非水溶媒系バインダ組成物とする。上記非水溶媒としては、例えば、溶解性が得られるものであればどのようなものでも良く、ジメチルアセトアミド、ジメチルホルムアミド、ジメチルスルホキシド、N-メチル-2-ピロリドン、γ-ブチロラクトン、スルホラン、シクロヘキサノン等が挙げられる。これらは単独で又は2種類以上を組み合わせて使用される。

【0039】本発明の非水溶媒系バインダ組成物と活物質とを混合し、電極基体表面に塗布し、極性非水溶媒を除去することにより電極を製造することができる。上記電極基体としては、例えば、アルミニウム、銅等が挙げられる。

【0040】上記活物質としては、公知のものを使用することができ、例えば、非晶質炭素、人造黒鉛等の炭素粉末などが挙げられるが、可逆的にリチウムイオンを挿入又は放出できる遷移金属酸化物であることが好ましく、これらの例としては、例えば、コバルト酸リチウム等のリチウムコバルト複合酸化物、ニッケル酸リチウム等のリチウムニッケル複合酸化物、マンガン酸リチウム等のリチウムマンガン複合酸化物、これらの混合物などが挙げられる。

【0041】上記リチウムニッケル複合酸化物において、Al、V、Cr、Fe、Co、Sr、Mo、W、Mn、B、Mg等から選ばれる少なくとも1種以上の金属でニッケルサイト又はリチウムサイトを置換したリチウムニッケル複合酸化物でも良い。上記リチウムマンガン複合酸化物においても、Li、Al、V、Cr、Fe、Co、Ni、Mo、W、Zn、B、Mgから選ばれる少なくとも1種以上の金属でマンガンサイト又はリチウムサイトを置換したリチウムマンガン複合酸化物でもよい。

【0042】上記リチウムマンガン複合酸化物は、 $Li_xMn_yO_z$ であることが好ましい。上記xは、 $0.2 \leq x \leq 2.5$ の範囲であることが好ましく、上記yは、 $0.8 \leq y \leq 1.25$ であることが好ましい。上記リチウムマンガン複合酸化物を正極活物質として用いて非水溶媒系二次電池を製造する場合、リチウムマンガン複合酸化物の粒子表面の一部を覆うように非水溶媒系バインダ組成物が存在するため、正極活物質から溶出するMn量を低減でき、正極の電子伝導性を確保し、一方で溶出したMnによる負極の劣化も抑制できるため、充放電サイクルによる電池容量低下を改善した有機電解液二次電池が得ることができる。

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【0043】上記電極を用いて非水溶媒系二次電池は、特に制限はないが、例えば、ポリエチレン微多孔膜等からなるセパレータを介して捲回し、スパイラル状の捲回群を作製し、この捲回群を電池缶に挿入し、予め負極集電体の銅箔に溶接しておいたニッケルタブ端子を電池缶底に溶接し、得られた電池容器に電解液を入れ、予め正極集電体のアルミニウム箔に溶接したアルミニウムタブ端子を蓋に溶接して、蓋を絶縁性のガスケットを介して電池缶の上部に配置させ、密閉するなどをして製造することができる。

【0044】上記電解液としては、例えば、カーボネート類、エステル類、エーテル類、ケトン類、ラクトン類、ニトリル類、アミン類、アミド類、硫黄化合物類、塩素化炭化水素類、スルホラン系化合物類等の有機溶媒が挙げられ、プロピレンカーボネート、エチレンカーボネート、1,2-ジメトキシエタン、1,2-ジエトキシエタン、ジエチルカーボネート、γ-ブチロラクトン、テトラヒドロフラン、ジエチルエーテル、スルホラン、アセトニトリル、ジメチルカーボネート、N-メチル-2-ピロリドン等の単独又は二種以上の混合溶媒が好ましい。上記電解質としては、例えば、 LiCl 、 LiPF_6 、 LiPF_4 、 LiBF_4 、 LiCl 、 LiBr 、 $\text{CH}_3\text{SO}_3\text{Li}$ 、 LiAsF_6 等が挙げられる。

【0045】本発明の電極は、活物質を含む合剤層と電極基体である金属箔との密着性に優れ、耐電解液性及び耐熱性に優れ、高温下で使用されても長期間電極基体と合剤層及び合剤層相互間の密着強度を維持できる。電極基体と合剤層及び合剤層相互間の密着強度が向上すると、合剤中の非水溶媒系バインダ組成物の添加量を低減でき、その結果活物質量を増やすことが可能で、この電極を用いた電池は体積エネルギー密度を増大できる。長期間電極基体と合剤層及び合剤層相互間の密着強度を維持

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*持した電極を用いた電池は、充放電を繰り返しても電極基体と合剤層及び合剤層相互間の導電ネットワークを維持でき、充電反応及び放電反応が均一に行えるので、サイクル寿命特性も向上できる。

【0046】

【実施例】以下、本発明を実施例に基づいて詳細に説明する。なお、例中特に断らない限り、部及び%はそれぞれ重量部及び重量%を示す。

【0047】(シロキサン変成ポリアミドイミド樹脂の合成) 逆流冷却器を連結したコック付き25ミリリットルの水分定量受器、温度計、攪拌器を備えた1リットルのセパラブルフラスコに芳香ジアミンとして2,2-ビス[4-(4-アミノフェノキシ)フェニル]プロパン、シロキサンジアミンとして反応性シリコーンオイルX-22-161-AS(信越化学工業株式会社製商品名、アミン当量416)、TMA(無水トリメリット酸)、非プロトン性極性溶媒としてNMP(N-メチル-2-ピロリドン)をそれぞれ表1に示した配合比で仕込み、80℃で30分間攪拌した。そして、水と共沸可能な芳香族炭化水素としてトルエン100ミリリットルを投入してから温度を上げ160℃で2時間還流させた。水分定量受器に水が3.6ミリリットル以上溜まっていること、水の流出が見られなくなっていることを確認し、水分定量受器に溜まっている流出水を除去しながら、約190℃まで温度を上げてトルエンを除去した。その後、溶液を室温に戻し、芳香族ジイソシアネートとしてMDI(4,4'-ジフェニルメタンジイソシアネート)を表1に示した量を投入し、190℃で2時間反応させた。反応終了後、シロキサン変成ポリアミドイミド樹脂A-1及びシロキサン変成ポリアミドイミド樹脂A-2のNMP溶液を得た。

【0048】

【表1】

表 1

試料名		A-1	A-2
配合(部)	BAPP ^{*1}	28.7	32.8
	X-22-161AS ^{*2}	58.3	16.6
	TMA ^{*3}	56.5	40.4
	NMP ^{*4}	383.6	307.3
	MDI ^{*5}	42.0	30.0
加熱残分(%)		32	26
重量平均分子量		63500	66000

*1: 2,2-ビス[4-(4-アミノフェノキシ)フェニル]プロパン

*2: 反応性シリコーンオイル(信越化学工業株式会社製商品名)、シロキサン系両末端アミン

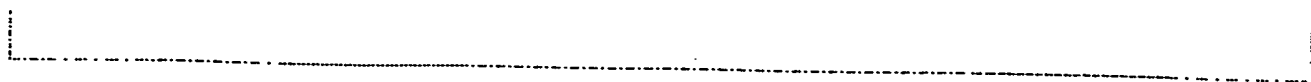
*3: 無水トリメリット酸

*4: N-メチル-2-ピロリドン

*5: 4,4'-ジフェニルメタンジイソシアネート

【0049】(非水溶媒系バインダ組成物の作製)
実施例1~6及び比較例1

得られたシロキサン変成ポリアミドイミド樹脂A-1及
50 シロキサン変成ポリアミドイミド樹脂A-2に対して



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表2に示す材料を加えバインダー用組成物を得た。得られたバインダー用樹脂組成物I～VI及び比較例1としてポリフッ化ビニリデンのN-メチル-2-ピロリドン溶液（呉羽化学製、商品名KF-1100）を乾燥膜厚約30 μ mとなるように圧延銅箔に塗布した後120℃で3時間乾燥し、180℃で2時間乾燥硬化させ、硬化塗膜を得た。次いで、予め両面テープを貼付けたガラス板に*

*硬化塗膜を貼付け、ガラス板に貼り付けた圧延銅箔接着硬化塗膜を得た。この硬化塗膜の接着性（圧延銅箔に対するピール強度）を測定した。その結果を表2に示した。

【0050】

【表2】

表 2

(単位部)

試 料 名		実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	比較例1
		非水溶媒系バインダー組成物						比較樹脂
		I	II	III	IV	V	VI	
(A) 成 分	シロキサン変性アミドイミド樹脂A-1 (固形分92%)	313	313	313	313	313	-	-
	シロキサン変性アミドイミド樹脂A-2 (固形分26%)	-	-	-	-	-	385	-
	ポリフッ化ビニリデン樹脂 (固形分12%)	-	-	-	-	-	-	833 (固形分100)
(B) 成 分	ビスフェノールA型エポキシ ：エポトート8125 *6	40	50	60	50	50	50	-
	エポキシ化ポリブタジエン ：エポリードPB3600 *7	10	10	10	5	15	10	-
	2-エチル-4-メチルイミダゾール	0.2	0.2	0.2	0.2	0.2	0.2	-
接 着 性		ピール強度 (N/m)						
		1	0.9	0.8	0.9	1.1	0.9	0.5

*6：東都化成株式会社商品名

*7：ダイセル化学株式会社商品名

【0051】（負極電極の作製）

実施例7

平均粒径20 μ mの非晶質炭素と非水溶媒系バインダー組成物Iを96：4の割合で混合し、N-メチル-2-ピロリドンに投入混合して、スラリー状の溶液を作製する。厚み10 μ mの銅箔の両面にこの溶液を塗布、乾燥する。台剤塗布量は片面65 q/m^2 である。台剤かさ密度が1.0 q/cm^2 になるように、ロールプレス機で圧延し、56mm幅に切断して短細状の負極台剤電極シートを作製した。負極台剤電極シートの端部にニッケル製の集電タブを超音波溶着し、その後、電極内の残留溶媒、吸着水の除去及び非水溶媒系バインダー組成物の架橋のため、180℃で1時間真空乾燥して負極台剤電極を得た。

【0052】実施例8～12

スラリー状の溶液の作製時に非水溶媒系バインダー組成物II～VIを用いる以外は実施例7と同様にして負極電極を得た。

【0053】実施例13

平均粒径20 μ mの人造黒鉛と非水溶媒系バインダー組成物Iを95：5の割合で混合し、N-メチル-2-ピロリドンに投入混合して、スラリー状の溶液を作製する。

厚み10 μ mの銅箔の両面にこの溶液を塗布、乾燥する。台剤塗布量は片面65 q/m^2 である。台剤かさ密度が1.0 q/cm^2 になるように、ロールプレス機で圧延し、56mm幅に切断して短細状の負極台剤電極シートを作製した。負極台剤電極シートの端部にニッケル製の集電タブを超音波溶着し、その後、電極内の残留溶媒、吸着水の除去及び非水溶媒系バインダー組成物の架橋のため、180℃で1時間真空乾燥して負極台剤電極を得た。

【0054】実施例14～18

スラリー状の溶液の作製時に非水溶媒系バインダー組成物II～VIを用いる以外は実施例13と同様にして負極電極を得た。

【0055】比較例2

負極は平均粒径20 μ mの非晶質炭素とポリフッ化ビニリデン樹脂とを90：10の割合で混合し、N-メチル-2-ピロリドンに投入混合して、スラリー状の溶液を作製する。厚み10 μ mの銅箔の両面にこの溶液を塗布、乾燥する。台剤塗布量は片面65 q/m^2 である。台剤かさ密度が1.0 q/cm^2 になるように、ロールプレス機で圧延し、56mm幅に切断して短細状の負極台剤電極シートを作製した。負極台剤電極シートの端部にニッケル

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製の集電タブを超音波溶着し、その後、電極内の残留溶媒や吸着水の除去及びバインダ樹脂の熱硬化のため、160℃で3時間真空乾燥して負極合剤電極を得た。

【0056】比較例3

非水溶媒系バインダ組成物に代わってポリフッ化ビニリデン樹脂を用いる以外は実施例13と同様にして負極電極を得た。

【0057】得られた電極について、耐電解液性（電解*

＊液として、N-メチル-2-ピロリドン、または、濃度が1MとなるようにLiPF₆を溶解させたエチレンカーボネート/ジメチルカーボネート=1/2（体積比）の混合液を用い、これらに50℃で24時間浸漬後の電子顕微鏡による倍率1000倍における外観異常の有無）を評価した。これらの結果を表3に示した。

【0058】

【表3】

表 3

	使用した非水溶媒系バインダ組成物	電解液A *8	電解液B *9
実施例7	非水溶媒系バインダ組成物 I	外観異常なし	外観異常なし
実施例8	非水溶媒系バインダ組成物 II	外観異常なし	外観異常なし
実施例9	非水溶媒系バインダ組成物 III	外観異常なし	外観異常なし
実施例10	非水溶媒系バインダ組成物 IV	外観異常なし	外観異常なし
実施例11	非水溶媒系バインダ組成物 V	外観異常なし	外観異常なし
実施例12	非水溶媒系バインダ組成物 VI	外観異常なし	外観異常なし
実施例13	非水溶媒系バインダ組成物 I	外観異常なし	外観異常なし
実施例14	非水溶媒系バインダ組成物 II	外観異常なし	外観異常なし
実施例15	非水溶媒系バインダ組成物 III	外観異常なし	外観異常なし
実施例16	非水溶媒系バインダ組成物 IV	外観異常なし	外観異常なし
実施例17	非水溶媒系バインダ組成物 V	外観異常なし	外観異常なし
実施例18	非水溶媒系バインダ組成物 VI	外観異常なし	外観異常なし
比較例2	ポリフッ化ビニリデンのN-メチル-2-ピロリドン溶液（呉羽化学製、商品名BF-1109）	表面膨潤	表面膨潤
比較例3	ポリフッ化ビニリデンのN-メチル-2-ピロリドン溶液（呉羽化学製、商品名BF-1101）	表面膨潤	表面膨潤

*8：電解液A（濃度が1モル/リットルとなるようにLiPF₆を溶解させたプロピレンカーボネートの混合液）

*9：電解液B（濃度が1モル/リットルとなるようにLiPF₆を溶解させたエチレンカーボネート/ジメチルカーボネート=1/2（体積比）の混合液）

【0059】得られた負極合剤電極の単極による初回の30%の充放電試験を行い、これを繰り返すことでサイクル特充電容量、放電容量及び不可逆容量を放電電流0.28

mA/cm²、制限電圧5mVで定電圧充電した後、放電電流

0.28mA/cm²で放電終止電圧1Vに至るまで放電させ※

【0060】

【表4】

表 4

	初 回		
	充電容量 (mAh/g)	放電容量 (mAh/g)	不可逆容量 (mAh/g)
実施例7	384	351	33
実施例8	387	354	33
実施例9	385	353	32
実施例10	386	354	32
実施例11	383	349	34
実施例12	380	345	35
実施例13	401	368	33

【0061】

【表5】

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表 5

	初 回		
	充電容量 (mAh/g)	放電容量 (mAh/g)	不可逆容量 (mAh/g)
実施例14	405	370	35
実施例15	405	370	35
実施例16	400	367	33
実施例17	403	369	34
実施例18	395	360	35
比較例2	360	295	65
比較例3	370	300	70

【0062】(リチウム二次電池の作製)

実施例19

正極活物質として LiCoO_2 を89重量%、導電剤として平均粒径が $1\mu\text{m}$ の鱗片状天然黒鉛を8重量%及び結着剤として非水溶媒系バインダ樹脂組成物Iを3重量%添加して、これにN-メチル-2-ピロリドンを加え混合して正極合剤のスラリーを調整した。同様に負極物質として平均粒径 $12\mu\text{m}$ の非晶質炭素95重量%及び結着剤として非水溶媒系バインダ樹脂組成物Iを5重量%添加して、これにN-メチル-2-ピロリドンを加え混合して負極合剤のスラリーを得た。次に正極合剤のスラリーを厚みが $25\mu\text{m}$ のアルミニウム箔の両面に塗布し、その後 120°C で1時間真空乾燥した。真空乾燥後、ローラプレスにより電極を加圧成形して厚みを $190\mu\text{m}$ とした。単位面積当たりの正極結着剤塗布量は、 $49\text{mg}/\text{cm}^2$ であり、幅が 40mm で長さが 285mm の大きさに切り出して正極を作製した。ただし、正極の両端の長さ 10mm の部分は正極合剤が塗布されておらずアルミニウム箔が露出しており、この一方に正極タブを超音波接合によって圧着した。

【0063】一方、負極合剤のスラリーを厚みが $10\mu\text{m}$ の銅箔の両面に塗布し、その後 120°C で1時間真空乾燥した。真空乾燥後、ローラプレスにより電極を加圧成形して厚みを $175\mu\text{m}$ とした。単位面積当たりの正極結着剤塗布量は、 $20\text{mg}/\text{cm}^2$ であり、幅が 40mm で長さが 290mm の大きさに切り出して負極を作製した。これを正極と同様に、負極の両端の長さ 10mm の部分は負極合剤が塗布されておらず銅箔が露出しており、この一方に負極タブを超音波接合によって圧着した。セパレータは、厚みが $25\mu\text{m}$ で幅が 44mm のポリエチレン製の微孔膜を用いた。

【0064】次いで、正極、セパレータ、負極及びセパレータの順で重ね合わせ、これを捲回して電極群とした。これを単三サイズの電池缶に挿入して、負極タブを缶底溶接し、正極蓋をかきしめるための絞り部を設けた。この後体積比で1:1のエチレンカーボネートとジエチルカーボネートの混合溶媒に六フッ化リン酸リチウムを1モル/リットル溶解させた電解液を電池缶に注入した

後、正極タブを正極蓋に溶接し、その後、正極蓋をかきしめリチウム二次電池を得た。

【0065】得られたリチウム二次電池を用い、充放電サイクル特性を評価した。作製したリチウム二次電池の充電は、電流 300mA で電池電圧 4.2V まで定電流で充電した後、電池電圧 4.2V で電流が 30mA になるまで定電圧電流で充電した。放電は、電流 300mA で電池電圧 2.8V になるまで定電流放電を行った。この充放電サイクルを300回繰り返した。表6に1サイクル目の放電容量、100サイクル目及び300サイクル目の放電容量維持率を示す。

【0066】実施例20~24

正極及び負極の結着剤にバインダ用樹脂II~IVを用いる以外は実施例19と同様にしてリチウム二次電池を作製し、実施例19と同様に充放電サイクル特性を評価した。表6に1サイクル目の放電容量、100サイクル目及び300サイクル目の放電容量維持率を示す。

【0067】実施例25

負極活物質に平均粒径 20nm の人造黒鉛を用いる以外は、実施例19と同様にしてリチウム二次電池を作製し、実施例19と同様に充放電サイクル特性を評価した。表6に1サイクル目の放電容量、100サイクル目及び300サイクル目の放電容量維持率を示す。

【0068】実施例26~30

正極及び負極の結着剤にバインダ用樹脂II~IVを用いる以外は実施例25と同様にしてリチウム二次電池を作製し、実施例25と同様に充放電サイクル特性を評価した。表6に1サイクル目の放電容量、100サイクル目及び300サイクル目の放電容量維持率を示す。

【0069】比較例4

正極の結着剤にポリフッ化ビニリデン樹脂を5重量%、負極の結着剤にポリフッ化ビニリデンを10重量%用いる以外は実施例19と同様にしてリチウム二次電池を作製し、実施例19と同様に充放電サイクル特性を評価した。表6に1サイクル目の放電容量100サイクル目及び300サイクル目の放電容量維持率を示す。

【0070】比較例5

正極の結着剤にポリフッ化ビニリデンを5重量%、負極



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の結着剤にポリフッ化ビニリデンを10重量%用いる以外は実施例25と同様にしてリチウム二次電池を作製し実施例25と同様に充放電サイクル特性を評価した。表6に1サイクル目の放電容量、100サイクル目及び3*

*00サイクル目の放電容量維持率を示す。

【0071】

【表6】

表 6

試料名	正極活物質	負極活物質	正・負極結着剤	1サイクル目放電容量 (mAh)	100サイクル目放電容量維持率 (%)	300サイクル目放電容量維持率 (%)
実施例19	LiCoO_2	非晶質炭素	非水溶媒系バインダ組成物 I	532	93	89
実施例20	LiCoO_2	非晶質炭素	非水溶媒系バインダ組成物 II	535	93	88
実施例21	LiCoO_2	非晶質炭素	非水溶媒系バインダ組成物 III	536	94	89
実施例22	LiCoO_2	非晶質炭素	非水溶媒系バインダ組成物 IV	538	95	90
実施例23	LiCoO_2	非晶質炭素	非水溶媒系バインダ組成物 V	533	93	89
実施例24	LiCoO_2	非晶質炭素	非水溶媒系バインダ組成物 VI	535	94	90
比較例4	LiCoO_2	非晶質炭素	ポリフッ化ビニリデン樹脂	420	88	76
実施例25	LiCoO_2	人造黒鉛	非水溶媒系バインダ組成物 I	620	89	83
実施例26	LiCoO_2	人造黒鉛	非水溶媒系バインダ組成物 II	623	88	84
実施例27	LiCoO_2	人造黒鉛	非水溶媒系バインダ組成物 III	625	88	83
実施例28	LiCoO_2	人造黒鉛	非水溶媒系バインダ組成物 IV	630	90	85
実施例29	LiCoO_2	人造黒鉛	非水溶媒系バインダ組成物 V	615	87	82
実施例30	LiCoO_2	人造黒鉛	非水溶媒系バインダ組成物 VI	625	88	84
比較例5	LiCoO_2	人造黒鉛	ポリフッ化ビニリデン樹脂	510	85	21

【0072】

【発明の効果】請求項1記載の非水溶媒系バインダ組成物は、接着性、屈曲性及び耐電解液性が優れ、非水溶媒系二次電池の電極に極めて有用である。請求項2記載の非水溶媒系バインダ組成物は、請求項1記載の発明の効果に加えて、さらに接着性及び耐熱性が優れ、非水溶媒系二次電池の電極に極めて有用である。請求項3記載の非水溶媒系バインダ組成物は、請求項1又は2記載の発明の効果を奏し、さらに耐熱性が優れ、非水溶媒系二次電池の電極に極めて有用である。

【0073】請求項4記載の非水溶媒系バインダ組成物は、請求項1、2又は3記載の発明の効果を奏し、さらに耐熱性及び耐電解液性が優れ、非水溶媒系二次電池の電極に極めて有用である。請求項5記載の非水溶媒系バインダ組成物は、請求項4記載の発明の効果を奏し、さらに耐熱性及び耐電解液性が優れ、非水溶媒系二次電池の電極に極めて有用である。請求項6記載の電極の製造法は、接着性、屈曲性、耐電解液性、電池にしたときの※

※サイクル寿命特性及び高温下での接着性が優れ、非水溶媒系二次電池に極めて有用である。

【0074】請求項7記載の電極の製造法は、請求項6記載の発明の効果を奏し、さらに電池にしたときのサイクル寿命特性が優れ、非水溶媒系二次電池に極めて有用である。請求項8記載の電極の製造法は、請求項7記載の発明の効果を奏し、さらに電池にしたときのサイクル寿命特性が優れ、非水溶媒系二次電池に極めて有用である。

【0075】請求項9記載の電極は、接着性、屈曲性、耐電解液性、電池にしたときのサイクル寿命特性及び高温下での接着性が優れ、活物質の増量に有効で体積エネルギー密度を増大することができる。請求項10記載の非水溶媒系二次電池の製造法は、サイクル寿命特性、耐電解液性及び高温下での接着性が優れ、活物質の増量に有効で体積エネルギー密度を増大することができ、破裂・爆発危険性が小さく、安全性が高い。

フロントページの続き

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CLAIMS

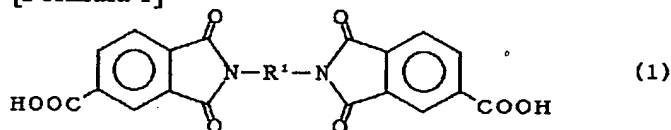
[Claim(s)]

[Claim 1] (A) The non-aqueous-solvent system binder constituent which made the non-aqueous solvent dissolve or distribute a siloxane denaturation polyamidoimide resin.

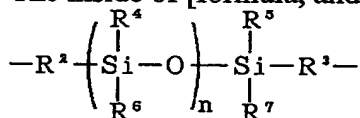
[Claim 2] (A) The non-aqueous-solvent system binder constituent according to claim 1 whose siloxane denaturation polyamidoimide resin of a component is a siloxane denaturation polyamidoimide resin which mixture, a multiple-valued carboxylic acid, or diisocyanate with a siloxane diamine, an aromatic diamine, or an aliphatic diamine is made to react, and is obtained.

[Claim 3] (A) The general formula from which the siloxane denaturation polyamidoimide resin of a component makes mixture and trimellitic anhydride with a siloxane diamine, an aromatic diamine, or an aliphatic diamine react, and is obtained (1)

[Formula 1]



The inside of [formula, and R1. [Formula 2]



(-- a formula -- inside -- R -- two -- and -- R -- three -- each -- independent -- divalent -- organic -- a machine -- being shown -- R -- four -- R -- five -- R -- six -- and -- R -- seven -- each -- independent -- a carbon number -- one -- -- 20 -- an alkyl group -- a carbon number -- six -- -- 18 -- an aryl group -- being shown -- n -- one -- -- 50 -- an integer -- it is --) -- it is --]

[Claim 4] The non-aqueous-solvent system binder constituent according to claim 1, 2, or 3 which made the non-aqueous solvent dissolve or distribute (B) thermosetting resin furthermore.

[Claim 5] (B) The non-aqueous-solvent system binder constituent according to claim 4 whose thermosetting resin of a component is an epoxy resin which has two or more glycidyl groups.

[Claim 6] The manufacturing method of the electrode characterized by mixing a non-aqueous-solvent system binder constituent and an active material according to claim 1, 2, 3, 4, or 5, and removing a non-aqueous solvent after applying to an electrode base front face.

[Claim 7] The manufacturing method of the electrode according to claim 6 whose active material is the transition-metals oxide which can insert or emit a lithium ion in reversible by charge and discharge.

[Claim 8] The manufacturing method of the electrode according to claim 7 which is the lithium manganese multiple oxide a transition-metals oxide is indicated to be by the general formula Li_xMnyO_2 (the range of x is $0.2 \leq x \leq 2.5$, and the range of y is $0.8 \leq y \leq 1.25$).

[Claim 9] The electrode manufactured according to the manufacturing method of an electrode according to claim 6, 7, or 8.

[Claim 10] The non-aqueous-solvent system rechargeable battery which used the electrode according to claim 9 for one [at least] pole of a non-aqueous-solvent system rechargeable battery.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to a non-aqueous-solvent system binder constituent, the manufacturing method of an electrode, an electrode, and a non-aqueous-solvent system rechargeable battery.

[0002]

[Description of the Prior Art] By progress of electronic technology, the performance of electronic equipment improves, small and portable-ization progress, and a cell of high-energy density is desired as a power supply. As a conventional rechargeable battery, although a lead accumulator, nickel, and a cadmium cell are mentioned, it is still inadequate in that a cell with a high energy density is obtained. Then, as what is replaced with these cells, the organic electrolytic-solution rechargeable battery (it is described as a lithium secondary battery below) of high-energy density is developed, and it has spread quickly.

[0003] After a carbon material with little fear of the deposit of flexibility and a lithium which occlusion discharge of a lithium was possible for and was excellent is used for a negative electrode in lithium compound metallic oxides, such as a lithium cobalt multiple oxide, in a positive electrode, and a lithium secondary battery carries out the double spread of what the N-methyl-2-pyrrolidone (NMP) was made to distribute these and a binder resin, and was made into the slurry on the metallic foil which is a charge collector and dries a solvent, it is pressed with a roller-press machine. Positive and the negative-electrode board have been obtained. Many polyvinylidene fluorides (PVDF) are mainly used as a binder.

[0004] However, since adhesion of the interface of a charge collector and a binder layer and the adhesion between binder layers are inferior when a polyvinylidene fluoride is used as a binder, at the time of manufacturing processes, such as a decision process, a winding process, etc. of a plate, some mixtures exfoliate and are omitted from a charge collector, and it becomes a very small short circuit and the cause of cell capacity dispersion. Moreover, in order to expand and contract especially the carbon material of a negative electrode by repeating charge and discharge, there was a problem that a mixture exfoliates and is omitted from a charge collector, or the ununiformity of decline in current collection efficiency and a reaction with a lithium arose, and cell capacity fell gradually by the fall of adhesion between mixtures.

[0005] The monomer and unsaturation dibasicity monoester which furthermore make the fluoride vinylidene of a publication a principal component at JP,6-172452,A are copolymerized. When using the obtained fluoride vinylidene system copolymer as a binder, although the adhesion intensity with a charge collector improved, the abnormal-temperature rise under the high voltage decomposed, hydrogen fluoride was generated, and it reacted with the lithium intercalation compound (GIC) of a negative-electrode board front face, or the depositing metal lithium, carried out unusual generation of heat, and had a possibility that a cell might explode and explode.

[0006] The proposal which uses thermoplastics, such as polyimide resin given in synthetic rubber and

JP,6-163031,A containing styrene-butadiene-rubber (SBR) system synthetic rubber given in JP,5-74461,A and diene system rubber given in JP,9-87571,A, as binders other than fluororesins, such as a polyvinylidene fluoride, is made. However, it dissolves to the electrolytic solution, or these are swollen greatly, and cannot maintain adhesion of the interface of a charge collector and a binder layer, and adhesion between binder layers for a long period of time. Moreover, in case the electrode which flexibility was low and produced is wound even if it forms a binder layer when using polyimide resin, the crack of a binder layer and exfoliation arise and capacity is reduced. Although it has electrolytic-solution-proof nature, uniform distribution of an active material, a binder, etc. is very difficult, a cellulose, a surfactant, etc. need to be added, these dissolve in the electrolytic solution, and diene system synthetic rubber, such as styrene butadiene rubber, reduces the charge-and-discharge efficiency of a cell.

[0007]

[Problem(s) to be Solved by the Invention] Invention according to claim 1 is excellent in an adhesive property, flexibility, and electrolytic-solution-proof nature, and provides the electrode of a non-aqueous-solvent system rechargeable battery with a very useful non-aqueous-solvent system binder constituent. In addition to an effect of the invention according to claim 1, invention according to claim 2 is further excellent in an adhesive property and thermal resistance, and provides the electrode of a non-aqueous-solvent system rechargeable battery with a very useful non-aqueous-solvent system binder constituent. Invention according to claim 3 does so an effect of the invention according to claim 1 or 2, and thermal resistance is further excellent, and it provides the electrode of a non-aqueous-solvent system rechargeable battery with a very useful non-aqueous-solvent system binder constituent.

[0008] Invention according to claim 4 does so an effect of the invention according to claim 1, 2, or 3, and thermal resistance and electrolytic-solution-proof nature are further excellent, and it provides the electrode of a non-aqueous-solvent system rechargeable battery with a very useful non-aqueous-solvent system binder constituent. Invention according to claim 5 does so an effect of the invention according to claim 4, and thermal resistance and electrolytic-solution-proof nature are further excellent, and it provides the electrode of a non-aqueous-solvent system rechargeable battery with a very useful non-aqueous-solvent system binder constituent. Invention according to claim 6 is excellent in the cycle-life property when making it an adhesive property, flexibility, electrolytic-solution-proof nature, and a cell, and the adhesive property under an elevated temperature, and provides a non-aqueous-solvent system rechargeable battery with the manufacturing method of a very useful electrode.

[0009] invention according to claim 7 does so an effect of the invention according to claim 6, and the cycle-life property when making it a cell further is excellent, and it provides a non-aqueous-solvent ** rechargeable battery with the manufacturing method of a very useful electrode invention according to claim 8 does so an effect of the invention according to claim 7, and the cycle-life property when making it a cell further is excellent, and it provides a non-aqueous-solvent ** rechargeable battery with the manufacturing method of a very useful electrode

[0010] Invention according to claim 9 is excellent in the cycle-life property when making it an adhesive property, flexibility, electrolytic-solution-proof nature, and a cell, and the adhesive property under an elevated temperature, is effective in increase in quantity of an active material, and offers the electrode which can increase a volume energy density. Invention according to claim 10 is excellent in a cycle-life property, electrolytic-solution-proof nature, and the adhesive property under an elevated temperature, it can be effective in increase in quantity of an active material, and a volume energy density can be increased, burst / explosion danger is small and safety offers the manufacturing method of a high non-aqueous-solvent system rechargeable battery.

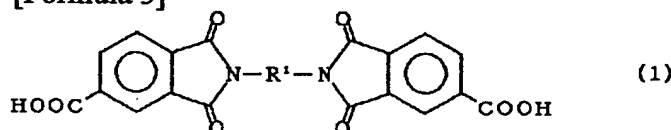
[0011]

[Means for Solving the Problem] this invention relates to the non-aqueous-solvent system binder constituent which made the non-aqueous solvent dissolve or distribute (A) siloxane denaturation

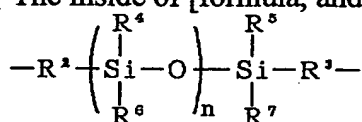
polyamidoimide resin. Moreover, this invention relates to the aforementioned non-aqueous-solvent system binder constituent whose siloxane denaturation polyamidoimide resin of the (A) component is a siloxane denaturation polyamidoimide resin which mixture, a multiple-valued carboxylic acid, or diisocyanate with a siloxane diamine, an aromatic diamine, or an aliphatic diamine is made to react, and is obtained.

[0012] Moreover, this invention is a general formula (1) from which the siloxane denaturation polyamidoimide resin of the (A) component makes mixture and trimellitic anhydride with a siloxane diamine, an aromatic diamine, or an aliphatic diamine react, and is obtained.

[Formula 3]



The inside of [formula, and R1. [Formula 4]



(-- the inside of a formula, and R2 and R3 -- each -- an independently divalent organic machine -- being shown -- R4, R5, R6, and R7 -- each -- the alkyl group of carbon numbers 1-20 and the aryl group of carbon numbers 6-18 are shown independently, and n is the integer of 1-50 -- it is related with the aforementioned non-aqueous-solvent system binder constituent which is the siloxane denaturation polyamidoimide resin which diisocyanate is made to react to the reactant containing the diimide dicarboxylic acid shown

[0013] Moreover, this invention relates to the aforementioned non-aqueous-solvent system binder constituent which made the non-aqueous solvent dissolve or distribute (B) thermosetting resin further. Moreover, this invention relates to the aforementioned non-aqueous-solvent system binder constituent whose thermosetting resin of the (B) component is an epoxy resin which has two or more glycidyl groups. Moreover, this invention mixes the aforementioned non-aqueous-solvent system binder constituent and an active material, and relates to the manufacturing method of the electrode characterized by removing a non-aqueous solvent after applying to an electrode base front face.

[0014] Moreover, this invention relates to the manufacturing method of the aforementioned electrode whose active material is the transition-metals oxide which can insert or emit a lithium ion in reversible by charge and discharge. Moreover, this invention relates to the manufacturing method of the aforementioned electrode which is the lithium manganese multiple oxide a transition-metals oxide is indicated to be by the general formula $\text{Li}_x\text{M}_y\text{O}_2$ (the range of x is $0.2 \leq x \leq 2.5$, and the range of y is $0.8 \leq y \leq 1.25$).

[0015] Moreover, this invention relates to the electrode manufactured according to the manufacturing method of the aforementioned electrode. Moreover, this invention relates to the non-aqueous-solvent system rechargeable battery which used the aforementioned electrode for one [at least] pole of a non-aqueous-solvent system rechargeable battery.

[0016]

[Embodiments of the Invention] The non-aqueous-solvent system binder constituent of this invention needs to make a non-aqueous solvent dissolve or distribute (A) siloxane denaturation polyamidoimide resin.

[0017] The mole ratio of the number of sum total mols of the mixture (**/**=50/50 - 100 / 0 mole ratios) of for example, ** siloxane diamine, ** aromatic diamine, or an aliphatic diamine, a multiple-valued carboxylic acid, or diisocyanate can make the siloxane denaturation polyamidoimide resin (above-mentioned [A]) able to react by 1 / 2.20 - 1/2.05, and can obtain it. As for the mole ratio of

the above-mentioned **/**, it is desirable that it is 50 / 50 - 100/0, and it is more desirable that it is 70 / 30 - 100/0. There is an inclination for an adhesive property to fall [this mole ratio] less than by 50/50.

[0018] As for the mole ratio of the number of sum total mols of the mixture of the aforementioned ** siloxane diamine, ** aromatic diamine, or an aliphatic diamine, a multiple-valued carboxylic acid, or diisocyanate, it is desirable that it is 1 / 2.20 - 1/2.05, and it is more desirable that it is 1 / 2.15 - 1/2.10. When there is an inclination for an adhesive property to fall [this mole ratio] less than by 1/2.20 and 1/2.05 is exceeded, there is an inclination for thermal resistance to fall.

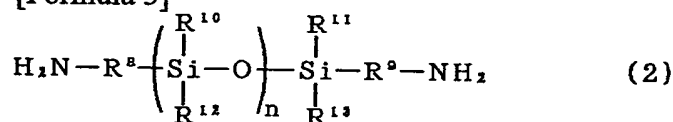
[0019] Moreover, as for the siloxane denaturation polyamidoimide resin (aforementioned [A]), it is desirable that it is the siloxane denaturation polyamidoimide resin which diisocyanate is made to react to the reactant containing the diimide dicarboxylic acid shown by the general formula (1) which mixture and trimellitic anhydride with a siloxane diamine, an aromatic diamine, or an aliphatic diamine are made to react, and is obtained, and is obtained.

[0020] As a divalent organic machine, arylene machines, such as alkylene machines, such as a methylene group, an ethylene, and a propylene machine, a phenylene group, a tolylene machine, and a KISHIRIREN machine, etc. are mentioned among the aforementioned general formula (1), for example. As an alkyl group of carbon numbers 1-20, among the aforementioned general formula (1) For example, a methyl group, an ethyl group, n-propyl group, an isopropyl machine, n-butyl, An isobutyl machine, a sec-butyl, a tert-butyl, a pentyl machine, An isopentyl machine, a neopentyl machine, a hexyl machine, a heptyl machine, an octyl machine, A nonyl machine, a decyl group, a undecyl machine, a dodecyl machine, a tridecyl machine, a tetradecyl machine, a pentadecyl group, a hexadecyl machine, a heptadecyl machine, an octadecyl machine, a nona decyl group, icosyl groups, these structural isomers, etc. are mentioned. Among the aforementioned general formula (1), as an aryl group of carbon numbers 6-18, a phenyl group, a tolyl group, a xylyl group, a biphenyl machine, a naphthyl group, an anthryl machine, a phenan tolyl group, etc. may be mentioned, and it may be replaced by a halogen atom, the amino group, a nitro group, the cyano group, the sulfhydryl group, the allyl group, the alkyl group of carbon numbers 1-20, etc., for example.

[0021] As for the mole ratio of the siloxane diamine for obtaining the diimide dicarboxylic acid shown by the aforementioned general formula (1), and trimellitic anhydride, it is desirable that it is 1 / 2.20 - 1/2.05, and it is more desirable that it is 1 / 2.15 - 1/2.10. Subsequently, the diimide dicarboxylic acid and diisocyanate which are shown by the aforementioned general formula (1) are made to react by the mole ratio 1 / 1.50 - 1/1.05, things are desirable, and it is more desirable to make it react by 1 / 1.35 - 1/1.20.

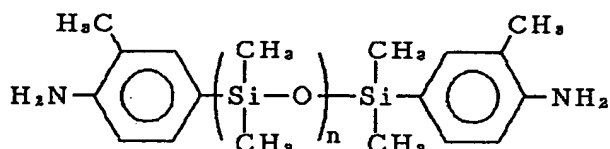
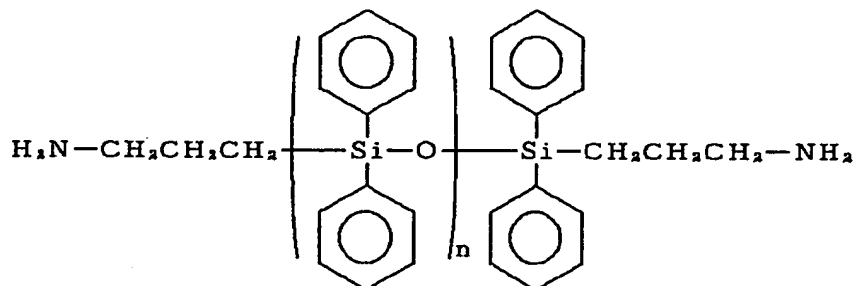
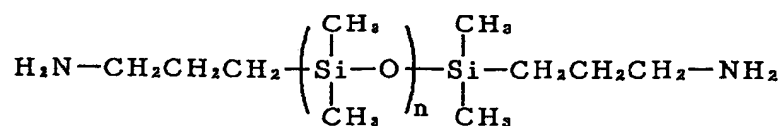
[0022] As the aforementioned siloxane diamine, it is a general formula (2), for example.

[Formula 5]



What is expressed with (R8 and R9 show a divalent organic machine independently respectively among a formula, R10, R11, R12, and R13 show the alkyl group of carbon numbers 1-20 and the aryl group of carbon numbers 6-18 independently respectively, and n is the integer of 1-50) is used.

[0023] As such a siloxane diamine, it is the following formula. [Formula 6]



What is shown for the (inside of a formula and n to be the integers) of 1-50 is mentioned.

[0024] Amino denaturation silicone-oil X-22-161AS which is a siloxane system both-ends amine also in these as an available thing commercially, for example (the amine equivalent 450, tradename by Shin-Etsu Chemical Co., Ltd.), X-22-161A (the amine equivalent 840, tradename by Shin-Etsu Chemical Co., Ltd.), X-22-161B (the amine equivalent 1500, tradename by Shin-Etsu Chemical Co., Ltd.), BY 16-853 (the amine equivalent 650, Dow Corning Toray Silicone tradename), BY16-853B (the amine equivalent 2200, Dow Corning Toray Silicone tradename), etc. are mentioned. a siloxane diamine -- the inside of a diamine from the point of an adhesive property and flexibility -- more than 50 mol % -- using is desirable These are independent or are used combining two or more kinds.

[0025] As the aforementioned aromatic diamine, for example O-phenylenediamine, m-phenylenediamine, p-phenylene diamine, 3, and 3'-diamino diphenyl-ether, 4, and 4'-diamino diphenyl-ether, 3, 4'-diamino diphenyl-ether, 3, and 3'-diamino diphenyl difluoromethane, 4, A 4'-diamino diphenyl fluoro methane, 3, and 3'-diaminodiphenyl-sulfone, 3, 4'-diaminodiphenyl-sulfone, 4, and 4'-diaminodiphenyl-sulfone, 3, and 3'-diamino diphenyl sulfide, 3, a 4'-diamino diphenyl sulfide, 4, 4'-diamino diphenyl sulfide, 3, and 3'-diamino diphenyl-ketone, 3, 4'-diamino diphenyl-ketone, 4, and 4'-diamino diphenyl SURUKETON, 2, and 2-screw (3-aminophenyl) propane, 2, and 2-(3, 4'-diamino diphenyl) propane, 2 and 2- Hexafluoro propane, 2, and 2-screw (4-aminophenyl) hexafluoro propane, 1, 3-screw (3-amino phenoxy) benzene 1, 4-screw (4-amino phenoxy) benzene, 3, 3'-[1, 4-phenylene screw (3, 4'-diamino diphenyl)] screw aniline, 3, 4'-[1 and 4-phenylene screw (1-methyl ethylidene)] screw aniline, 4, and 4'-[1 and 4-phenylene screw (1-methyl ethylidene)] screw aniline, 2, and 2-screw [4- (1-methyl ethylidene) A phenyl] propane, 2, (3-amino phenoxy) 2-screw [4- Phenyl] propane, 2, and 2-screw [4-(3-amino phenoxy) phenyl] hexafluoro propane, 2, and 2-screw [4-(4-amino phenoxy) phenyl] hexafluoro propane, screw [4- (4-amino phenoxy) (3-amino phenoxy) A phenyl] sulfide, a screw [4-(3-amino phenoxy) phenyl] sulfone, a screw [4-(4-amino phenoxy) phenyl] sulfone, etc. are mentioned. It is desirable that it is what has three or more aromatic rings also in these. These are independent or are used combining two or more kinds.

[0026] As the aforementioned aliphatic diamine, there are an alkylene diamine, a polyoxyalkylene diamine, etc., for example. Moreover, heterocycle formula diamines, such as alicyclic diamines [, such as isophorone diamine, 4 and 4'-dicyclohexyl methanediamine,], 3, and 9-screw (3-aminopropyl)-SUPIRO [2, 4, 8, and 10-tetrapod] [5, 5] undecane, etc. are mentioned. These are independent or are used combining two or more kinds. As for the ratio of an aromatic diamine and an

aliphatic diamine, it is desirable to use from a heat-resistant point at 20 or less % of the weight to the total quantity of an aromatic diamine / aliphatic diamine.

[0027] As the aforementioned multiple-valued carboxylic acid, for example Oxalic acid, a malonic acid, a succinic acid, A glutaric acid, an adipic acid, a pimelic acid, an azelaic acid, a sebacic acid, ARUKIRENTE-Tell joint content dicarboxylic acids, such as dodecane 2 acid and eicosane 2 acid, Aliphatic dicarboxylic acids, such as an alkylene carbonate joint content dicarboxylic acid and a butadiene joint content dicarboxylic acid, Aromatic dicarboxylic acids, such as a phthalic acid, an isophthalic acid, a terephthalic acid, and a naphthalene dicarboxylic acid, Butane - 1, 2, 4-tricarboxylic acid, naphthalene - 1, 2, 4-tricarboxylic acid, Tricarboxylic acids, such as trimellitic acid, butane - 1, 2, 3, 4-tetracarboxylic acid, Pyromellitic acid, benzophenone -3, 3', 4, and 4'-tetracarboxylic acid, Tricarboxylic acids, such as diphenyl-ether -3, 3', 4, and 4'-tetracarboxylic acid, Biphenyl -3, 3', 4, and 4'-tetracarboxylic acid, naphthalene [- Carboxylic acids, such as 1, 2 5, and 8-tetracarboxylic acid, an anhydrous TORIMETTO acid etc. are mentioned.] - 2, 3, 6, 7-tetracarboxylic acid, naphthalene - 1, 2, 4, 5-tetracarboxylic acid, naphthalene As for an aliphatic dicarboxylic acid, it is desirable to use less than [20 mol %] in a multiple-valued carboxylic acid from a heat-resistant point. These are independent or are used combining two or more kinds.

[0028] As the aforementioned aromatic diisocyanate, for example 4 and 4'-diphenylmethane diisocyanate (It abbreviates to MDI hereafter), 2, 4-tolylene diisocyanate, 2, 6-tolylene diisocyanate, 1, 5-naphthalene diisocyanate, tolidine di-isocyanate, p-phenyl diisocyanate, 4-4'-diphenyletherdiisocyanate, Aromatic diisocyanate, such as m-xylylene diisocyanate and m-tetramethyl xylylene diisocyanate, 1, 6-hexamethylene di-isocyanate, 2 and 2, 4-trimethylhexamethylene JIISHI cyanate, Cycloaliphatic diisocyanate, such as aliphatic diisocyanate [, such as 2, 4, and 4-trimethylhexamethylene JIISHI cyanate,], isophorone diisocyanate, 4, and 4'-dicyclohexylmethane diisocyanate, etc. is mentioned. As for aliphatic diisocyanate, it is desirable to use less than [10 mol %] from a heat-resistant point. These are independent or are used combining two or more kinds.

[0029] The siloxane denaturation polyamidoimide resin of the (A) component used by this invention For example, mixture ((I)/(II) = 0.1/99.9 - 99.9 / 0.1 mole ratios) and trimellitic anhydride of an aromatic diamine or an aliphatic diamine (I), and a siloxane diamine (II) The number of sum total mols of ((I)+ (II)) and the mole ratio of TMA (it abbreviates to TMA hereafter) by 1 / 2.20 - 1/2.05 under existence of a non-proton nature polar solvent Make it react at about 50-90 degrees C for about 0.2 to 1.5 hours, and the aromatic hydrocarbon in which water and azeotropy are still more possible is supplied by about 0.1 - 0.5% of the weight of the non-proton nature polar solvent. React at 120-180 degrees C, and the mixture containing siloxane diimide dicarboxylic acid is manufactured. This and aromatic diisocyanate (III) can be manufactured at reacting at about 150-250 degrees C for about 0.5 to 3 hours ((III) = 1/1.50 - 1 / 1.05 mole ratios) ((I) + (II)). Moreover, after manufacturing aromatic diimide dicarboxylic acid, an aromatic hydrocarbon can be removed from the solution by making the solution into about 150-250 degrees C, and it can also manufacture by performing the reaction of this and aromatic diisocyanate. Moreover, as for a siloxane denaturation polyamidoimide resin, it is desirable that it is a varnish containing a non-proton nature polar solvent.

[0030] It is desirable that they are a siloxane diamine and TMA, and the organic solvent that does not react as the aforementioned non-proton nature polar solvent, for example, in order to mention a dimethylacetamide, a dimethylformamide, dimethyl sulfoxide, a N-methyl-2-pyrrolidone, gamma-butyrolactone, a sulfolane, a cyclohexanone, etc. and for an imide-ized reaction to take an elevated temperature, especially a N-methyl-2-pyrrolidone with the high boiling point is desirable. Since a reaction does not fully advance but the moisture content contained in the above-mentioned non-proton nature polar solvent causes [of a polymer] a molecular weight fall by the trimellitic acid which TMA hydrates and generates, it is desirable to be managed at 0.2 or less % of the weight. Moreover, although not restricted, that the solubility of TMA falls and it becomes impossible to perform sufficient reaction when there are many rates of a weight with which a siloxane diamine and

TMA were doubled, and since [if conversely low,] it is disadvantageous as a industrial manufacturing method, a bird clapper is desirable [especially the non-proton nature polar solvent used by this invention] in 10 - 70% of the weight of the range. These are independent or are used combining two or more kinds.

[0031] As for the weight average molecular weight of (A) siloxane denaturation polyamidoimide resin of this invention, it is desirable that it is 30,000-100,000 from the balance of a property, and it is more desirable that it is 45,000-85,000. When there is an inclination for thermal resistance to fall [this weight average molecular weight] less than by 30,000 and 100,000 is exceeded, there is an inclination for an adhesive property to fall. In this invention, weight average molecular weight is measured using the calibration curve by standard polystyrene by the gel permeation chromatography method (GPC).

[0032] The non-aqueous-solvent system binder constituent of this invention can be made to contain (B) thermosetting resin if needed. As the above-mentioned thermosetting resin, an epoxy resin, phenol resin, polyester resin, polyimide resin, a bismaleimide triazine resin, etc. are mentioned, for example.

[0033] Especially the epoxy resin from the point of an adhesive property and handling nature is desirable. as the above-mentioned epoxy resin For example, the bisphenol A type epoxy resin, a bisphenol female mold epoxy resin, A bisphenol S type epoxy resin, a phenol novolak type epoxy resin, A cresol novolak type epoxy resin, a naphthalene type epoxy resin, and its denaturation object, BIKISHIRE nil diglycidyl ether, YDC1312 (Tohto Kasei make), TMH574 (Sumitomo Chemical make), Epicoat 1031S (product made from oil-ized shell), Aromatic system epoxy resins, such as EPOTOTO 8125 (tradename by Tohto Kasei Co., Ltd.), Neopentyl glycol diglycidyl ether, polypropylene glycol diglycidyl ether, Heterocycle formula epoxy compounds, such as aliphatic system epoxy resins, such as tetrahydrophtal acid diglycidyl ester, and a triglycidyl isocyanate, EPOLEAD PB3600 (tradename made from Die Cell Chemistry), etc. are mentioned.

[0034] In these, it is desirable to use the epoxy resin which has two or more glycidyl groups, and its hardening accelerator. Moreover, a glycidyl group is so good that there are, and if it is three or more pieces, it is still more desirable. [many] Loadings change with number of glycidyl groups, and the loadings to a silicone denaturation polyamidoimide resin are so good that there are many glycidyl groups at least. Moreover, it is still more desirable if the curing agent of an epoxy resin is used together. These are independent or are used combining two or more kinds.

[0035] As for the loadings of the epoxy resin used by this invention, it is desirable that it is the 5 - 100 weight section to an adhesive property, flexibility, and a heat-resistant point to the (A) component 100 weight section, and it is more desirable that it is 10 - 50 weight section. When there is an inclination for electrolytic-solution-proof nature with these loadings sufficient in under 5 weight sections not to be obtained and the 100 weight sections are exceeded, there is an inclination for a sufficient adhesive property and sufficient flexibility not to be obtained.

[0036] As the curing agent or hardening accelerator of the aforementioned epoxy resin, in an epoxy resin, the thing which reacts, or hardening, if it is a promotion ***** thing, what thing may be used, for example, amines, imidazole derivatives, polyfunctional phenols, and acid anhydrides will be mentioned. As the above-mentioned amines, a dicyandiamide, a diamino diphenylmethane, a guanylurea, etc. are mentioned, for example. As the above-mentioned imidazole derivatives, alkyl group substitution imidazoles, such as a 2-ethyl-4-methyl imidazole, a benzimidazole, etc. are mentioned, for example. As the above-mentioned polyfunctional phenols, novolak phenol type phenol resin, resole type phenol resin, etc. which are a hydroquinone, a resorcinol, bisphenol A and these halogenated compounds, and the addition condensation object of the aforementioned polyfunctional phenols and formaldehyde are mentioned, for example. As the above-mentioned acid anhydrides, phthalic anhydride, a benzophenone tetracarboxylic acid dihydrate, methyl himic acid, etc. are mentioned, for example. Among these, as a hardening accelerator, especially the thing for which imidazole derivatives are used is desirable.

[0037] In the case of amines, the initial complement of these curing agents or a hardening accelerator has the desirable amount to which the equivalent of the active hydrogen of an amine and the weight per epoxy equivalent of an epoxy resin become almost equal. In the case of an imidazole, it does not become equivalent ratio with active hydrogen simply, but it is [0.1 - 10.0 weight section] experimentally necessary to the epoxy resin 100 weight section. In the case of polyfunctional phenols, 0.6 to 1.2 hydroxyl equivalent is required to 1Eq of epoxy groups of an epoxy resin. Since a non-hardened epoxy resin remains if there are few amounts of these curing agents or a hardening accelerator, an adhesive property falls, and since an unreacted curing agent and an unreacted hardening accelerator remain if many [too], electrolytic-solution-proof nature falls. These are independent or are used combining two or more kinds.

[0038] In this invention, a non-aqueous solvent is made to dissolve or distribute these constituents so that a solid content may become about 10 - 30% of the weight, and it considers as a non-aqueous-solvent system binder constituent. As the above-mentioned non-aqueous solvent, if solubility is acquired, what thing may be used and a dimethylacetamide, a dimethylformamide, dimethyl sulfoxide, a N-methyl-2-pyrrolidone, gamma-butyrolactone, a sulfolane, a cyclohexanone, etc. will be mentioned, for example. These are independent or are used combining two or more kinds.

[0039] The non-aqueous-solvent system binder constituent and active material of this invention can be mixed, it can apply to an electrode base front face, and an electrode can be manufactured by removing a polar non-aqueous solvent. As the above-mentioned electrode base, aluminum, copper, etc. are mentioned, for example.

[0040] Although a well-known thing can be used as the above-mentioned active material, for example, the end of a carbon powder, such as an amorphous carbon and an artificial graphite, etc. is mentioned, it is desirable that it is the transition-metals oxide which can insert or emit a lithium ion in reversible, and lithium manganese multiple oxides, such as lithium nickel multiple oxides, such as lithium cobalt multiple oxides, such as a cobalt acid lithium, and a nickel acid lithium, and a manganic acid lithium, such mixture, etc. are mentioned as these examples, for example.

[0041] In the above-mentioned lithium nickel multiple oxide, the lithium nickel multiple oxide which replaced the nickel site or the lithium site with at least one or more sorts of metals chosen from aluminum, V, Cr, Fe, Co, Sr, Mo, W, Mn, B, Mg, etc. is sufficient. Also in the above-mentioned lithium manganese multiple oxide, the lithium manganese multiple oxide which replaced the manganese site or the lithium site with at least one or more sorts of metals chosen from Li, aluminum, V, Cr, Fe, Co, nickel, Mo, W, Zn, B, and Mg is sufficient.

[0042] As for the above-mentioned lithium manganese multiple oxide, it is desirable that it is $\text{Li}_x\text{Mn}_y\text{O}_2$. As for Above x, it is desirable that it is the range of $0.2 \leq x \leq 2.5$, and it is [Above y] desirable that it is $0.8 \leq y \leq 1.25$. The amount of Mn eluted from a positive active material since a non-aqueous-solvent system binder constituent exists so that a part of particle front face of a lithium manganese multiple oxide may be worn when manufacturing a non-aqueous-solvent system rechargeable battery, using the above-mentioned lithium manganese multiple oxide as a positive active material can be reduced, the electronic-conduction nature of a positive electrode is secured, and since degradation of the negative electrode by Mn eluted in one side can also be suppressed, the organic electrolytic-solution rechargeable battery which has improved the cell capacity fall by the charge-and-discharge cycle can obtain.

[0043] Although especially a limit does not have a non-aqueous-solvent system rechargeable battery using the above-mentioned electrode For example, it winds through the separator which consists of a polyethylene fine porous membrane etc. Produce a spiral-like winding group, insert this winding group in a cell can, and the nickel tab terminal beforehand welded to the copper foil of a negative-electrode charge collector is welded to a battery can bottom. The electrolytic solution is put into the obtained cell container, and the aluminum tab terminal beforehand welded to the aluminum foil of a positive-electrode charge collector is welded to a lid, and a lid can be arranged in the upper part of a cell can through an insulating gasket, and it can carry out sealing etc. and can manufacture.

[0044] As the above-mentioned electrolytic solution, for example, organic solvents, such as carbonate, ester, ether, ketones, lactone, nitril, amines, amides, sulfur compounds, chlorinated hydrocarbons, and sulfolane system compounds, are mentioned, and independent or two or more kinds of mixed solvents, such as propylene carbonate, ethylene carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, diethyl carbonate, gamma-butyrolactone, a tetrahydrofuran, diethylether, a sulfolane, an acetonitrile, dimethyl carbonate, and a N-methyl-2-pyrrolidone, are desirable As the above-mentioned electrolyte, LiClO₄, LiPF₆, LiPF₄, LiBF₄, LiCl, LiBr, CH₃SO₃Li, and LiAsF₆ grade are mentioned, for example.

[0045] The electrode of this invention is excellent in the adhesion of the binder layer containing an active material, and the metallic foil which is an electrode base, excellent in electrolytic-solution-proof nature and thermal resistance, and even if used under an elevated temperature, it can maintain an electrode base, a binder layer, and the adhesion intensity between binder layers for a long period of time. if an electrode base, a binder layer, and the adhesion intensity between binder layers improve -- a mixture -- the addition of an inner non-aqueous-solvent system binder constituent can be reduced, it is possible to, increase the amount of active materials as a result, and the cell using this electrode can increase a volume energy density Since the cell using the electrode which maintained an electrode base, a binder layer, and the adhesion intensity between binder layers for a long period of time can maintain an electrode base, a binder layer, and the electric conduction network between binder layers and can perform a charge reaction and an electric discharge reaction uniformly even if it repeats charge and discharge, its cycle-life property can also improve.

[0046]

[Example] Hereafter, this invention is explained in detail based on an example. In addition, unless it refuses especially among an example, the section and % show weight section and weight %, respectively.

[0047] (Composition of a siloxane conversion polyamidoimide resin) with [which connected the reflux condenser] a cock -- the 1l. separable flask equipped with the 25ml moisture fixed quantity receiver, the thermometer, and the stirrer -- as an aroma diamine as 2 and 2-screw [4-(4-amino phenoxy) phenyl] propane and a siloxane diamine -- reactant silicone-oil X-22-161- it taught with the compounding ratio which showed NMP (N-methyl-2-pyrrolidone) in Table 1, respectively as AS (the tradename by Shin-Etsu Chemical Co., Ltd., amine equivalent 416), TMA (trimellitic anhydride), and a non-proton nature polar solvent, and agitated for 30 minutes at 80 degrees C And after supplying 100ml of toluene as an aromatic hydrocarbon in which water and azeotropy are possible, temperature was raised and it was made to flow back at 160 degrees C for 2 hours. It checked that 3.6ml or more of water has collected on a moisture fixed quantity receiver, and that the outflow of water was no longer seen, and removing an effluent collected on the moisture fixed quantity receiver, temperature was raised to about 190 degrees C, and toluene was removed. Then, the solution was returned to the room temperature, the amount which showed MDI (4 and 4'-diphenylmethane diisocyanate) in Table 1 as aromatic diisocyanate was supplied, and it was made to react at 190 degrees C for 2 hours. The NMP solution of the siloxane conversion polyamidoimide resin A-1 and the siloxane conversion polyamidoimide resin A-2 was obtained after the reaction end.

[0048]

[Table 1]

表 1

試 料 名		A-1	A-2
配 合 (部)	BAPP ⁻¹	28.7	32.8
	X-22-161AS ⁻²	58.3	16.6
	TMA ⁻³	56.5	40.4
	NMP ⁻⁴	383.6	307.3
	MDI ⁻⁵	42.0	30.0

加 熱 残 分 (%)	32	26
重 量 平 均 分 子 量	63500	66000

- *1: 2, 2-ビス[4-(4-アミノフェノキシ)フェニル]プロパン
 *2: 反応性シリコンオイル (信越化学工業株式会社製商品名)、
 シロキサン系両末端アミン
 *3: 無水トリメリット酸
 *4: N-メチル-2-ピロリドン
 *5: 4, 4'-ジフェニルメタンジイソシアネート

[0049] (Production of a non-aqueous-solvent system binder constituent)

The material shown in Table 2 to examples 1-6, the siloxane conversion polyamidoimide resin A-1 obtained example of comparison 1, and the siloxane conversion polyamidoimide resin A-2 was added, and the constituent for binders was obtained. After applying the N-methyl-2-pyrrolidone solution (the product made from the Kureha chemistry, tradename KF-1100) of a polyvinylidene fluoride to rolling copper foil as obtained resin constituent I-VI for binders, and an example 1 of comparison so that it may become about 30 micrometers of dryness thickness, it dried at 120 degrees C for 3 hours, and dryness hardening was carried out at 180 degrees C for 2 hours, and the hardening paint film was obtained. Subsequently, the hardening paint film was stuck on the glass plate which stuck the double-sided tape beforehand, and the rolling copper foil adhesion hardening paint film stuck on the glass plate was obtained. The adhesive property (Peel intensity to rolling copper foil) of this hardening paint film was measured. The result was shown in Table 2.

[0050]

[Table 2]

		表 2						(重量部)
試 料 名		実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	比較例1
		非水溶媒系バインダ組成物						比較樹脂
		I	II	III	IV	V	VI	
(A) 成 分	シロキサン変性アミドイミド樹脂A-1 (固形分32%)	313	313	313	313	313	—	—
	シロキサン変性アミドイミド樹脂A-2 (固形分26%)	—	—	—	—	—	385	—
	ポリフッ化ビニリデン樹脂 (固形分12%)	—	—	—	—	—	—	833 (固形分100)
(B) 成 分	ビスフェノールA型エポキシ :エポトート8125 *6	40	50	60	50	50	50	—
	エポキシ化ポリブタジエン :エポリードPB3600 *7	10	10	10	5	15	10	—
	2-エチル-4-メチルイミダゾール	0.2	0.2	0.2	0.2	0.2	0.2	—
接 着 性		ピール強度 (KN/m)						
		1	0.9	0.8	0.9	1.1	0.9	0.5

*6: 東都化成株式会社商品名

*7: ダイセル化学株式会社商品名

[0051] (Production of a negative-electrode electrode)

The amorphous carbon of 20 micrometers of example 7 mean particle diameters and the non-aqueous-solvent system binder constituent I are mixed at a rate of 96:4, injection mixture is carried out at a N-methyl-2-pyrrolidone, and a slurry-like solution is produced. This solution is applied to both sides of copper foil with a thickness of 10 micrometers, and it dries to them. a mixture -- a

coverage is one side 65 g/m² a mixture -- bulk density becomes 1.0 g/cm³ -- as -- a roll-press machine -- rolling out -- 56mm width of face -- cutting -- a short **-like negative electrode -- a mixture -- the electrode sheet was produced a negative electrode -- a mixture -- the current collection tab of the product [edge / of an electrode sheet] made from nickel -- ultrasonic welding -- carrying out -- a bridge formation of removal of the remains solvent in after that and an electrode, and the water of adsorption, and a non-aqueous-solvent system binder constituent sake -- 180 degrees C -- a 1-hour vacuum drying -- carrying out -- a negative electrode -- a mixture -- the electrode was obtained

[0052] The negative-electrode electrode was obtained like the example 7 except using non-aqueous-solvent system binder constituent II-VI at the time of production of the solution of the shape of an example 8 - 12 slurries.

[0053] The non-aqueous-solvent system binder constituent I is mixed with the artificial graphite of 20 micrometers of example 13 mean particle diameters at a rate of 95:5, injection mixture is carried out at a N-methyl-2-pyrrolidone, and a slurry-like solution is produced. This solution is applied to both sides of copper foil with a thickness of 10 micrometers, and it dries to them. a mixture -- a coverage is one side 65 g/m² a mixture -- bulk density becomes 1.0 g/cm³ -- as -- a roll-press machine -- rolling out -- 56mm width of face -- cutting -- a short **-like negative electrode -- a mixture -- the electrode sheet was produced a negative electrode -- a mixture -- the current collection tab of the product [edge / of an electrode sheet] made from nickel -- ultrasonic welding -- carrying out -- the bridge formation of removal and the resin constituent for non-aqueous-solvent system binders by the remains solvent in after that and an electrode, and adsorption sake -- 180 degrees C -- a 1-hour vacuum drying -- carrying out -- a negative electrode -- a mixture -- the electrode was obtained

[0054] The negative-electrode electrode was obtained like the example 13 except using non-aqueous-solvent system binder constituent II-VI at the time of production of the solution of the shape of an example 14 - 18 slurries.

[0055] Example of comparison 2 negative electrode mixes the amorphous carbon of 20 micrometers of mean particle diameters, and a polyvinylidene-fluoride resin at a rate of 90:10, carries out injection mixture at a N-methyl-2-pyrrolidone, and produces a slurry-like solution. This solution is applied to both sides of copper foil with a thickness of 10 micrometers, and it dries to them. a mixture -- a coverage is one side 65 g/m² a mixture -- bulk density becomes 1.0 g/cm³ -- as -- a roll-press machine -- rolling out -- 56mm width of face -- cutting -- a short **-like negative electrode -- a mixture -- the electrode sheet was produced a negative electrode -- a mixture -- the current collection tab of the product [edge / of an electrode sheet] made from nickel -- ultrasonic welding -- carrying out -- a heat curing of the remains solvent in after that and an electrode, or a removal of the water of adsorption and a binder resin sake -- 160 degrees C -- a 3-hour vacuum drying -- carrying out -- a negative electrode -- a mixture -- the electrode was obtained

[0056] The negative-electrode electrode was obtained like the example 13 except using a polyvinylidene-fluoride resin instead of an example of comparison 3 non-aqueous-solvent system binder constituent.

[0057] About the obtained electrode, electrolytic-solution-proof nature (existence of the abnormalities in appearance in one 1000 times the scale factor of this according to the electron microscope after being 24-hour immersed at 50 degrees C to these using the mixed liquor of the ethylene carbonate / dimethyl carbonate = 1/2 (volume ratio) in which LiPF₆ was dissolved as the electrolytic solution so that a N-methyl-2-pyrrolidone or concentration might be set to 1M) was evaluated. These results were shown in Table 3.

[0058]

[Table 3]

表 3

	使用した非水溶媒系バインダ組成物	電解液 A *8	電解液 B *9
実施例 7	非水溶媒系バインダ組成物 I	外観異常なし	外観異常なし
実施例 8	非水溶媒系バインダ組成物 II	外観異常なし	外観異常なし
実施例 9	非水溶媒系バインダ組成物 III	外観異常なし	外観異常なし
実施例 10	非水溶媒系バインダ組成物 IV	外観異常なし	外観異常なし
実施例 11	非水溶媒系バインダ組成物 V	外観異常なし	外観異常なし
実施例 12	非水溶媒系バインダ組成物 VI	外観異常なし	外観異常なし
実施例 13	非水溶媒系バインダ組成物 I	外観異常なし	外観異常なし
実施例 14	非水溶媒系バインダ組成物 II	外観異常なし	外観異常なし
実施例 15	非水溶媒系バインダ組成物 III	外観異常なし	外観異常なし
実施例 16	非水溶媒系バインダ組成物 IV	外観異常なし	外観異常なし
実施例 17	非水溶媒系バインダ組成物 V	外観異常なし	外観異常なし
実施例 18	非水溶媒系バインダ組成物 VI	外観異常なし	外観異常なし
比較例 2	ポリフッ化ビニリデンのN-メチル-2-ピロリドン溶液 (呉羽化学製、商品名KF-1100)	表面膨潤	表面膨潤
比較例 3	ポリフッ化ビニリデンのN-メチル-2-ピロリドン溶液 (呉羽化学製、商品名KF-1101)	表面膨潤	表面膨潤

*8: 電解液A (濃度が1モル/リットルとなるようにLiPF₆を溶解させたプロピレンカーボネートの混合液)

*9: 電解液B (濃度が1モル/リットルとなるようにLiPF₆を溶解させたエチレンカーボネート/ジメチルカーボネート=1/2 (体積比) の混合液)

[0059] the obtained negative electrode -- a mixture -- the charge and discharge test made to discharge until it results in neglect final-voltage 1V in discharge current 0.28 mA/cm², after carrying out constant-potential charge of the charge capacity, service capacity, and irreversible capacity of the first time by the single electrode of an electrode by discharge current 0.28 mA/cm² and 5mV of discharge voltage was performed, and the cycle property was measured by repeating this The result was shown in Table 4 and 5.

[0060]

[Table 4]

表 4

	初 回		
	充電容量 (mAh/g)	放電容量 (mAh/g)	不可逆容量 (mAh/g)
実施例 7	384	351	33
実施例 8	387	354	33
実施例 9	385	353	32
実施例 10	386	354	32
実施例 11	383	349	34
実施例 12	380	345	35
実施例 13	401	368	33

[0061]

[Table 5]

表 5

	初 回		
	充電容量 (mAh/g)	放電容量 (mAh/g)	不可逆容量 (mAh/g)
実施例14	405	370	35
実施例15	405	370	35
実施例16	400	367	33
実施例17	403	369	34
実施例18	395	360	35
比較例2	360	295	65
比較例3	370	300	70

[0062] (Production of a lithium secondary battery)

the scale-like natural graphite whose mean particle diameter is 1 micrometer as example 19 positive active material considering LiCoO_2 as 89 % of the weight and an electric conduction agent -- 8 % of the weight and a binder -- carrying out -- the non-aqueous-solvent system binder resin constituent I -- 3 % of the weight -- adding -- this -- a N-methyl-2-pyrrolidone -- adding -- mixing -- a positive electrode -- the slurry of a mixture was adjusted the same -- as the negative-electrode matter -- as 95 % of the weight of amorphous carbons of 12 micrometers of mean particle diameters, and a binder -- the non-aqueous-solvent system binder resin constituent I -- 5 % of the weight -- adding -- this -- a N-methyl-2-pyrrolidone -- adding -- mixing -- a negative electrode -- the slurry of a mixture was obtained next, a positive electrode -- thickness applied the slurry of a mixture to both sides of the aluminum foil which is 25 micrometers, and carried out the vacuum drying at 120 degrees C after that for 1 hour After the vacuum drying, pressing of the electrode was carried out with the roller press, and thickness was set to 190 micrometers. The positive-electrode binder coverage per unit area was 49 mg/cm², and width of face started it by 40mm in the size whose length is 285mm, and it produced the positive electrode. however, a portion with a length [of the ends of a positive electrode] of 10mm -- a positive electrode -- a mixture was not applied, but the aluminum foil was exposed, and the positive-electrode tab was stuck to one of these by pressure by ultrasonic jointing

[0063] on the other hand -- a negative electrode -- thickness applied the slurry of a mixture to both sides of the copper foil which is 10 micrometers, and carried out the vacuum drying at 120 degrees C after that for 1 hour After the vacuum drying, pressing of the electrode was carried out with the roller press, and thickness was set to 175 micrometers. The positive-electrode binder coverage per unit area was 20 mg/cm², and width of face started it by 40mm in the size whose length is 290mm, and it produced the negative electrode. this -- a positive electrode -- the same -- a portion with a length [of the ends of a negative electrode] of 10mm -- a negative electrode -- a mixture was not applied, but copper foil was exposed, and the negative-electrode tab was stuck to one of these by pressure by ultrasonic jointing As for separator, thickness used the micropore film made from polyethylene whose width of face is 44mm by 25 micrometers.

[0064] Subsequently, it piled up in order of a positive electrode, separator, a negative electrode, and separator, this was wound, and it considered as the electrode group. This was inserted in the cell can of single 3 sizes, can bottom welding of the negative-electrode tab was carried out, and the converging section for closing a positive-electrode lid was formed. After pouring into a cell can the electrolytic solution which dissolved one mol /of 6 fluoride [phosphoric-acid] lithiums in the mixed solvent of the ethylene carbonate and diethyl carbonate of 1:1 l. by the volume ratio after this, the positive-electrode tab was welded to the positive-electrode lid, and the caulking lithium secondary battery was obtained for the positive-electrode lid after that.

[0065] The charge-and-discharge cycle property was evaluated using the obtained lithium secondary

battery. Charge of the produced lithium secondary battery was charged with constant-voltage current until current was set to 30mA by cell-voltage 4.2V, after charging by the constant current to cell-voltage 4.2V with 300mA of current. Electric discharge performed constant-current discharge until it was set to cell-voltage 2.8V with 300mA of current. This charge-and-discharge cycle was repeated 300 times. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0066] Except using resin II-IV for binders for the binder of 20 to example 24 positive electrode, and a negative electrode, the lithium secondary battery was produced like the example 19, and the charge-and-discharge cycle property was evaluated like the example 19. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0067] Except using the artificial graphite of 20 microns of mean particle diameters for an example 25 negative-electrode active material, the lithium secondary battery was produced like the example 19, and the charge-and-discharge cycle property was evaluated like the example 19. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0068] Except using resin II-IV for binders for the binder of 26 to example 30 positive electrode, and a negative electrode, the lithium secondary battery was produced like the example 25, and the charge-and-discharge cycle property was evaluated like the example 25. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0069] Except using a polyvinylidene-fluoride resin for the binder of example of comparison 4 positive electrode, and using a polyvinylidene fluoride for the binder of a negative electrode 10% of the weight 5% of the weight, the lithium secondary battery was produced like the example 19, and the charge-and-discharge cycle property was evaluated like the example 19. The service-capacity maintenance factor of the service-capacity 100 cycle eye of 1 cycle eye and a 300 cycle eye is shown in Table 6.

[0070] Except using a polyvinylidene fluoride for the binder of example of comparison 5 positive electrode, and using a polyvinylidene fluoride for the binder of a negative electrode 10% of the weight 5% of the weight, the lithium secondary battery was produced like the example 25, and the charge-and-discharge cycle property was evaluated like the example 25. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0071]

[Table 6]

表 6

試料名	正極活物質	負極活物質	正・負極結着剤	1サイクル目 放電容量 (mAh)	100サイクル目放電 容量維持率 (%)	300サイクル目放電 容量維持率 (%)
実施例19	LiCoO ₂	非晶質炭素	非水溶媒系バイ ンダ組成物 I	532	93	89
実施例20	LiCoO ₂	非晶質炭素	非水溶媒系バイ ンダ組成物 II	535	93	88
実施例21	LiCoO ₂	非晶質炭素	非水溶媒系バイ ンダ組成物 III	536	94	89
実施例22	LiCoO ₂	非晶質炭素	非水溶媒系バイ ンダ組成物 IV	538	95	90
実施例23	LiCoO ₂	非晶質炭素	非水溶媒系バイ ンダ組成物 V	533	93	89
実施例24	LiCoO ₂	非晶質炭素	非水溶媒系バイ ンダ組成物 VI	535	94	90
比較例4	LiCoO ₂	非晶質炭素	ポリフッ化ビニ リデン樹脂	420	88	76
実施例25	LiCoO ₂	人造黒鉛	非水溶媒系バイ ンダ組成物 I	620	89	83
実施例26	LiCoO ₂	人造黒鉛	非水溶媒系バイ ンダ組成物 II	623	88	84
実施例27	LiCoO ₂	人造黒鉛	非水溶媒系バイ ンダ組成物 III	625	88	83
実施例28	LiCoO ₂	人造黒鉛	非水溶媒系バイ ンダ組成物 IV	630	90	85

実施例 29	LiCoO ₂	人造黒鉛	非水溶媒系バイ ンダ組成物 V	615	87	82
実施例 30	LiCoO ₂	人造黒鉛	非水溶媒系バイ ンダ組成物 VI	625	88	84
比較例 5	LiCoO ₂	人造黒鉛	ポリフッ化ビニ リデン樹脂	510	65	21

[0072]

[Effect of the Invention] A non-aqueous-solvent system binder constituent according to claim 1 is excellent in an adhesive property, flexibility, and electrolytic-solution-proof nature, and very useful to the electrode of a non-aqueous-solvent system rechargeable battery. In addition to an effect of the invention according to claim 1, a non-aqueous-solvent system binder constituent according to claim 2 is further excellent in an adhesive property and thermal resistance, and very useful to the electrode of a non-aqueous-solvent system rechargeable battery. A non-aqueous-solvent system binder constituent according to claim 3 does so an effect of the invention according to claim 1 or 2, and thermal resistance is further excellent, and it is very useful to the electrode of a non-aqueous-solvent system rechargeable battery.

[0073] A non-aqueous-solvent system binder constituent according to claim 4 does so an effect of the invention according to claim 1, 2, or 3, and thermal resistance and electrolytic-solution-proof nature are further excellent, and it is very useful to the electrode of a non-aqueous-solvent system rechargeable battery. A non-aqueous-solvent system binder constituent according to claim 5 does so an effect of the invention according to claim 4, and thermal resistance and electrolytic-solution-proof nature are further excellent, and it is very useful to the electrode of a non-aqueous-solvent system rechargeable battery. The manufacturing method of an electrode according to claim 6 is excellent in the cycle-life property when making it an adhesive property, flexibility, electrolytic-solution-proof nature, and a cell, and the adhesive property under an elevated temperature, and very useful to a non-aqueous-solvent system rechargeable battery.

[0074] The manufacturing method of an electrode according to claim 7 does so an effect of the invention according to claim 6, and the cycle-life property when making it a cell further is excellent, and it is very useful to a non-aqueous-solvent system rechargeable battery. The manufacturing method of an electrode according to claim 8 does so an effect of the invention according to claim 7, and the cycle-life property when making it a cell further is excellent, and it is very useful to a non-aqueous-solvent system rechargeable battery.

[0075] An electrode according to claim 9 is excellent in the cycle-life property when making it an adhesive property, flexibility, electrolytic-solution-proof nature, and a cell, and the adhesive property under an elevated temperature, can be effective in increase in quantity of an active material, and can increase a volume energy density. The manufacturing method of a non-aqueous-solvent system rechargeable battery according to claim 10 is excellent in a cycle-life property, electrolytic-solution-proof nature, and the adhesive property under an elevated temperature, can be effective in increase in quantity of an active material, can increase a volume energy density, is small, and is high. [of safety] [of burst / explosion danger]

[Translation done.]

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to a non-aqueous-solvent system binder constituent, the manufacturing method of an electrode, an electrode, and a non-aqueous-solvent system rechargeable battery.

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PRIOR ART

[Description of the Prior Art] By progress of electronic technology, the performance of electronic equipment improves, small and portable-ization progress, and a cell of high-energy density is desired as a power supply. As a conventional rechargeable battery, although a lead accumulator, nickel, and a cadmium cell are mentioned, it is still inadequate in that a cell with a high energy density is obtained. Then, as what is replaced with these cells, the organic electrolytic-solution rechargeable battery (it is described as a lithium secondary battery below) of high-energy density is developed, and it has spread quickly.

[0003] After a carbon material with little fear of the deposit of flexibility and a lithium which occlusion discharge of a lithium was possible for and was excellent is used for a negative electrode in lithium compound metallic oxides, such as a lithium cobalt multiple oxide, in a positive electrode, and a lithium secondary battery carries out the double spread of what the N-methyl-2-pyrrolidone (NMP) was made to distribute these and a binder resin, and was made into the slurry on the metallic foil which is a charge collector and dries a solvent, it is pressed with a roller-press machine. Positive and the negative-electrode board have been obtained. Many polyvinylidene fluorides (PVDF) are mainly used as a binder.

[0004] However, since adhesion of the interface of a charge collector and a binder layer and the adhesion between binder layers are inferior when a polyvinylidene fluoride is used as a binder, at the time of manufacturing processes, such as a decision process, a winding process, etc. of a plate, some mixtures exfoliate and are omitted from a charge collector, and it becomes a very small short circuit and the cause of cell capacity dispersion. Moreover, in order to expand and contract especially the carbon material of a negative electrode by repeating charge and discharge, there was a problem that a mixture exfoliates and is omitted from a charge collector, or the ununiformity of decline in current collection efficiency and a reaction with a lithium arose, and cell capacity fell gradually by the fall of adhesion between mixtures.

[0005] The monomer and unsaturation dibasicity monoester which furthermore make the fluoride vinylidene of a publication a principal component at JP,6-172452,A are copolymerized. When using the obtained fluoride vinylidene system copolymer as a binder, although the adhesion intensity with a charge collector improved, the abnormal-temperature elevation under the high voltage decomposed, hydrogen fluoride was generated, and it reacted with the lithium intercalation compound (GIC) of a negative-electrode board front face, or the depositing metal lithium, carried out unusual generation of heat, and had a possibility that a cell might explode and explode.

[0006] The proposal which uses thermoplastics, such as polyimide resin given in synthetic rubber and JP,6-163031,A containing styrene-butadiene-rubber (SBR) system synthetic rubber given in JP,5-74461,A and diene system rubber given in JP,9-87571,A, as binders other than fluororesins, such as a polyvinylidene fluoride, is made. However, it dissolves to the electrolytic solution, or these are swollen greatly, and cannot maintain adhesion of the interface of a charge collector and a binder layer, and adhesion between binder layers for a long period of time. Moreover, in case the electrode which flexibility was low and produced is wound even if it forms a binder layer when using polyimide resin, the crack of a binder layer and ablation arise and capacity is reduced. Although it has electrolytic-solution-proof nature, uniform distribution of an active material, a binder, etc. is very difficult, a cellulose, a surfactant, etc. need to be added, these dissolve in the electrolytic solution, and diene system synthetic rubber, such as styrene butadiene rubber, reduces the charge-and-discharge

efficiency of a cell.

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EFFECT OF THE INVENTION

[Effect of the Invention] A non-aqueous-solvent system binder constituent according to claim 1 is excellent in an adhesive property, flexibility, and electrolytic-solution-proof nature, and very useful to the electrode of a non-aqueous-solvent system rechargeable battery. In addition to an effect of the invention according to claim 1, a non-aqueous-solvent system binder constituent according to claim 2 is further excellent in an adhesive property and thermal resistance, and very useful to the electrode of a non-aqueous-solvent system rechargeable battery. A non-aqueous-solvent system binder constituent according to claim 3 does so an effect of the invention according to claim 1 or 2, and thermal resistance is further excellent, and it is very useful to the electrode of a non-aqueous-solvent system rechargeable battery.

[0073] A non-aqueous-solvent system binder constituent according to claim 4 does so an effect of the invention according to claim 1, 2, or 3, and thermal resistance and electrolytic-solution-proof nature are further excellent, and it is very useful to the electrode of a non-aqueous-solvent system rechargeable battery. A non-aqueous-solvent system binder constituent according to claim 5 does so an effect of the invention according to claim 4, and thermal resistance and electrolytic-solution-proof nature are further excellent, and it is very useful to the electrode of a non-aqueous-solvent system rechargeable battery. The manufacturing method of an electrode according to claim 6 is excellent in the cycle-life property when making it an adhesive property, flexibility, electrolytic-solution-proof nature, and a cell, and the adhesive property under an elevated temperature, and very useful to a non-aqueous-solvent system rechargeable battery.

[0074] The manufacturing method of an electrode according to claim 7 does so an effect of the invention according to claim 6, and the cycle-life property when making it a cell further is excellent, and it is very useful to a non-aqueous-solvent system rechargeable battery. The manufacturing method of an electrode according to claim 8 does so an effect of the invention according to claim 7, and the cycle-life property when making it a cell further is excellent, and it is very useful to a non-aqueous-solvent system rechargeable battery.

[0075] An electrode according to claim 9 is excellent in the cycle-life property when making it an adhesive property, flexibility, electrolytic-solution-proof nature, and a cell, and the adhesive property under an elevated temperature, can be effective in increase in quantity of an active material, and can increase a volume energy density. The manufacturing method of a non-aqueous-solvent system rechargeable battery according to claim 10 is excellent in a cycle-life property, electrolytic-solution-proof nature, and the adhesive property under an elevated temperature, can be effective in increase in quantity of an active material, can increase a volume energy density, is small, and is high. [of safety] [of rupture and explosion risk]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Invention according to claim 1 is excellent in an adhesive property, flexibility, and electrolytic-solution-proof nature, and provides the electrode of a non-aqueous-solvent system rechargeable battery with a very useful non-aqueous-solvent system binder constituent. In addition to an effect of the invention according to claim 1, invention according to claim 2 is further excellent in an adhesive property and thermal resistance, and provides the electrode of a non-aqueous-solvent system rechargeable battery with a very useful non-aqueous-solvent system binder constituent. Invention according to claim 3 does so an effect of the invention according to claim 1 or 2, and thermal resistance is further excellent, and it provides the electrode of a non-aqueous-solvent system rechargeable battery with a very useful non-aqueous-solvent system binder constituent.

[0008] Invention according to claim 4 does so an effect of the invention according to claim 1, 2, or 3, and thermal resistance and electrolytic-solution-proof nature are further excellent, and it provides the electrode of a non-aqueous-solvent system rechargeable battery with a very useful non-aqueous-solvent system binder constituent. Invention according to claim 5 does so an effect of the invention according to claim 4, and thermal resistance and electrolytic-solution-proof nature are further excellent, and it provides the electrode of a non-aqueous-solvent system rechargeable battery with a very useful non-aqueous-solvent system binder constituent. Invention according to claim 6 is excellent in the cycle-life property when making it an adhesive property, flexibility, electrolytic-solution-proof nature, and a cell, and the adhesive property under an elevated temperature, and provides a non-aqueous-solvent system rechargeable battery with the manufacturing method of a very useful electrode.

[0009] invention according to claim 7 does so an effect of the invention according to claim 6, and the cycle-life property when making it a cell further is excellent, and it provides a non-aqueous-solvent ** rechargeable battery with the manufacturing method of a very useful electrode invention according to claim 8 does so an effect of the invention according to claim 7, and the cycle-life property when making it a cell further is excellent, and it provides a non-aqueous-solvent ** rechargeable battery with the manufacturing method of a very useful electrode

[0010] Invention according to claim 9 is excellent in the cycle-life property when making it an adhesive property, flexibility, electrolytic-solution-proof nature, and a cell, and the adhesive property under an elevated temperature, is effective in increase in quantity of an active material, and offers the electrode which can increase a volume energy density. Invention according to claim 10 is excellent in a cycle-life property, electrolytic-solution-proof nature, and the adhesive property under an elevated temperature, it can be effective in increase in quantity of an active material, and a volume energy density can be increased, burst / explosion danger is small and safety offers the manufacturing method of a high non-aqueous-solvent system rechargeable battery.

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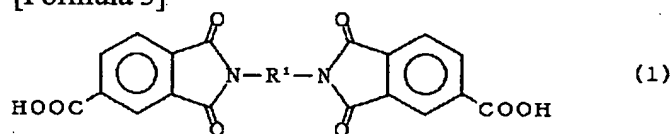
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MEANS

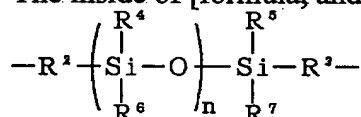
[Means for Solving the Problem] this invention relates to the non-aqueous-solvent system binder constituent which made the non-aqueous solvent dissolve or distribute (A) siloxane denaturation polyamidoimide resin. Moreover, this invention relates to the aforementioned non-aqueous-solvent system binder constituent whose siloxane denaturation polyamidoimide resin of the (A) component is a siloxane denaturation polyamidoimide resin which mixture, a multiple-valued carboxylic acid, or diisocyanate with a siloxane diamine, an aromatic diamine, or an aliphatic diamine is made to react, and is obtained.

[0012] Moreover, this invention is a general formula (1) from which the siloxane denaturation polyamidoimide resin of the (A) component makes mixture and trimellitic anhydride with a siloxane diamine, an aromatic diamine, or an aliphatic diamine react, and is obtained.

[Formula 3]



The inside of [formula, and R1. [Formula 4]



(-- the inside of a formula, and R2 and R3 -- each -- an independently divalent organic machine -- being shown -- R4, R5, R6, and R7 -- each -- the alkyl group of carbon numbers 1-20 and the aryl group of carbon numbers 6-18 are shown independently, and n is the integer of 1-50 -- it is related with the aforementioned non-aqueous-solvent system binder constituent which is the siloxane denaturation polyamidoimide resin which diisocyanate is made to react to the reactant containing the diimide dicarboxylic acid shown

[0013] Moreover, this invention relates to the aforementioned non-aqueous-solvent system binder constituent which made the non-aqueous solvent dissolve or distribute (B) thermosetting resin further. Moreover, this invention relates to the aforementioned non-aqueous-solvent system binder constituent whose thermosetting resin of the (B) component is an epoxy resin which has two or more glycidyl groups. Moreover, this invention mixes the aforementioned non-aqueous-solvent system binder constituent and an active material, and relates to the manufacturing method of the electrode characterized by removing a non-aqueous solvent after applying to an electrode base front face.

[0014] Moreover, this invention relates to the manufacturing method of the aforementioned electrode whose active material is the transition-metals oxide which can insert or emit a lithium ion in reversible by charge and discharge. Moreover, this invention relates to the manufacturing method of the aforementioned electrode which is the lithium manganese multiple oxide a transition-metals oxide is indicated to be by the general formula $\text{Li}_x\text{M}_y\text{O}_2$ (the range of x is $0.2 \leq x \leq 2.5$, and the range of y is $0.8 \leq y \leq 1.25$).

[0015] Moreover, this invention relates to the electrode manufactured according to the manufacturing method of the aforementioned electrode. Moreover, this invention relates to the non-aqueous-solvent

system rechargeable battery which used the aforementioned electrode for one [at least] pole of a non-aqueous-solvent system rechargeable battery.

[0016]

[Embodiments of the Invention] The non-aqueous-solvent system binder constituent of this invention needs to make a non-aqueous solvent dissolve or distribute (A) siloxane denaturation polyamidoimide resin.

[0017] The mole ratio of the number of sum total mols of the mixture (**/**=50/50 - 100 / 0 mole ratios) of for example, ** siloxane diamine, ** aromatic diamine, or an aliphatic diamine, a multiple-valued carboxylic acid, or diisocyanate can make the siloxane denaturation polyamidoimide resin (above-mentioned [A]) able to react by 1 / 2.20 - 1/2.05, and can obtain it. As for the mole ratio of the above-mentioned **/**, it is desirable that it is 50 / 50 - 100/0, and it is more desirable that it is 70 / 30 - 100/0. There is an inclination for an adhesive property to fall [this mole ratio] less than by 50/50.

[0018] As for the mole ratio of the number of sum total mols of the mixture of the aforementioned ** siloxane diamine, ** aromatic diamine, or an aliphatic diamine, a multiple-valued carboxylic acid, or diisocyanate, it is desirable that it is 1 / 2.20 - 1/2.05, and it is more desirable that it is 1 / 2.15 - 1/2.10. When there is an inclination for an adhesive property to fall [this mole ratio] less than by 1/2.20 and 1/2.05 is exceeded, there is an inclination for thermal resistance to fall.

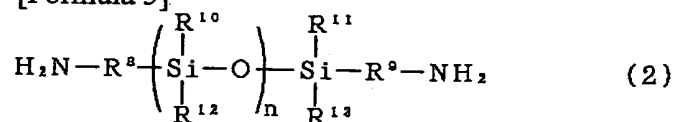
[0019] Moreover, as for the siloxane denaturation polyamidoimide resin (aforementioned [A]), it is desirable that it is the siloxane denaturation polyamidoimide resin which diisocyanate is made to react to the reactant containing the diimide dicarboxylic acid shown by the general formula (1) which mixture and trimellitic anhydride with a siloxane diamine, an aromatic diamine, or an aliphatic diamine are made to react, and is obtained, and is obtained.

[0020] As a divalent organic machine, arylene machines, such as alkylene machines, such as a methylene group, an ethylene, and a propylene machine, a phenylene group, a tolylene machine, and a xylylene machine, etc. are mentioned among the aforementioned general formula (1), for example. As an alkyl group of carbon numbers 1-20, among the aforementioned general formula (1) For example, a methyl group, an ethyl group, n-propyl group, an isopropyl machine, n-butyl, An isobutyl machine, a sec-butyl, a tert-butyl, a pentyl machine, An isopentyl machine, a neopentyl machine, a hexyl machine, a heptyl machine, an octyl machine, A nonyl machine, a decyl group, a undecyl machine, the dodecyl, a tridecyl machine, a tetradecyl machine, a pentadecyl group, a hexadecyl machine, a heptadecyl machine, an octadecyl machine, a nona decyl group, icosyl groups, these structural isomers, etc. are mentioned. Among the aforementioned general formula (1), as an aryl group of carbon numbers 6-18, a phenyl group, a tolyl group, a xylyl group, a biphenyl machine, a naphthyl group, an anthryl machine, a phenan tolyl group, etc. may be mentioned, and it may be replaced by a halogen atom, the amino group, a nitro group, the cyano group, the sulfhydryl group, the allyl group, the alkyl group of carbon numbers 1-20, etc., for example.

[0021] As for the mole ratio of the siloxane diamine for obtaining the diimide dicarboxylic acid shown by the aforementioned general formula (1), and trimellitic anhydride, it is desirable that it is 1 / 2.20 - 1/2.05, and it is more desirable that it is 1 / 2.15 - 1/2.10. Subsequently, the diimide dicarboxylic acid and diisocyanate which are shown by the aforementioned general formula (1) are made to react by the mole ratio 1 / 1.50 - 1/1.05, things are desirable, and it is more desirable to make it react by 1 / 1.35 - 1/1.20.

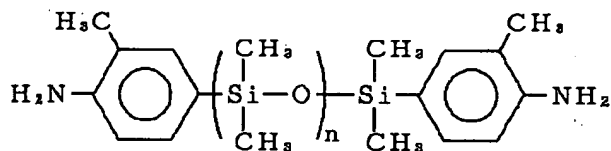
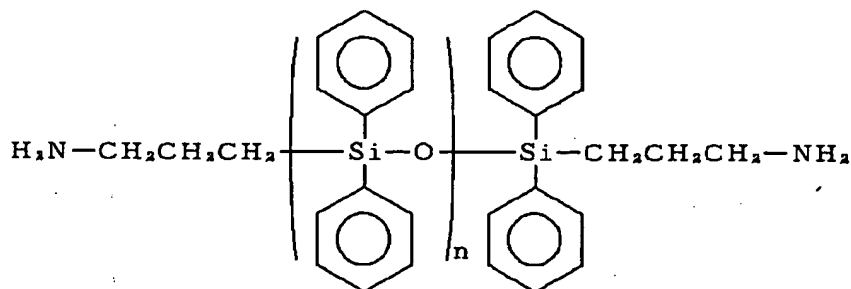
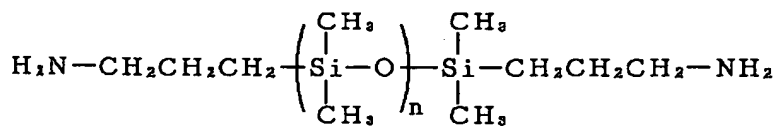
[0022] As the aforementioned siloxane diamine, it is a general formula (2), for example.

[Formula 5]



What is expressed with (R8 and R9 show a divalent organic machine independently respectively among a formula, R10, R11, R12, and R13 show the alkyl group of carbon numbers 1-20 and the aryl group of carbon numbers 6-18 independently respectively, and n is the integer of 1-50) is used.

[0023] As such a siloxane diamine, it is the following formula. [Formula 6]



What is shown for the (inside of a formula and n to be the integers) of 1-50 is mentioned.

[0024] Amino denaturation silicone-oil X-22-161AS which is a siloxane system both-ends amine also in these as an available thing commercially, for example (the amine equivalent 450, tradename by Shin-Etsu Chemical Co., Ltd.), X-22-161A (the amine equivalent 840, tradename by Shin-Etsu Chemical Co., Ltd.), X-22-161B (the amine equivalent 1500, tradename by Shin-Etsu Chemical Co., Ltd.), BY 16-853 (the amine equivalent 650, Dow Corning Toray Silicone tradename), BY16-853B (the amine equivalent 2200, Dow Corning Toray Silicone tradename), etc. are mentioned. a siloxane diamine -- the inside of a diamine from the point of an adhesive property and flexibility -- more than 50 mol % -- using is desirable These are independent or are used combining two or more kinds.

[0025] As the aforementioned aromatic diamine, for example O-phenylenediamine, m-phenylenediamine, p-phenylene diamine, 3, and 3'-diamino diphenyl-ether, 4, and 4'-diamino diphenyl-ether, 3, 4'-diamino diphenyl-ether, 3, and 3'-diamino diphenyl difluoromethane, 4, A 4'-diamino diphenyl fluoro methane, 3, and 3'-diaminodiphenyl-sulfone, 3, 4'-diaminodiphenyl-sulfone, 4, and 4'-diaminodiphenyl-sulfone, 3, and 3'-diamino diphenyl sulfide, 3, a 4'-diamino diphenyl sulfide, 4, 4'-diamino diphenyl sulfide, 3, and 3'-diamino diphenyl-ketone, 3, 4'-diamino diphenyl-ketone, 4, and 4'-diamino diphenyl SURUKETON, 2, and 2-screw (3-aminophenyl) propane, 2, and 2-(3, 4'-diamino diphenyl) propane, 2 and 2-Hexafluoro propane, 2, and 2-screw (4-aminophenyl) hexafluoro propane, 1, 3-screw (3-amino phenoxy) benzene 1, 4-screw (4-amino phenoxy) benzene, 3, 3'-[1, 4-phenylene screw (3, 4'-diamino diphenyl)] screw aniline, 3, 4'-[1 and 4-phenylene screw (1-methyl ethylidene)] screw aniline, 4, and 4'-[1 and 4-phenylene screw (1-methyl ethylidene)] screw aniline, 2, and 2-screw [4- (1-methyl ethylidene) A phenyl] propane, 2, (3-amino phenoxy) 2-screw [4- Phenyl] propane, 2, and 2-screw [4-(3-amino phenoxy) phenyl] hexafluoro propane, 2, and 2-screw [4-(4-amino phenoxy) phenyl] hexafluoro propane, screw [4- (4-amino phenoxy) (3-amino phenoxy) A phenyl] sulfide, a screw [4-(3-amino phenoxy) phenyl] sulfone, a screw [4-(4-amino phenoxy) phenyl] sulfone, etc. are mentioned. It is desirable that it is what has three or more aromatic rings also in these. These are independent or are used combining two or more kinds.

[0026] As the aforementioned aliphatic diamine, there are an alkylene diamine, a polyoxyalkylene diamine, etc., for example. Moreover, heterocycle formula diamines, such as alicyclic diamines [, such as isophorone diamine, 4 and 4'-dicyclohexyl methanediamine,], 3, and 9-screw (3-aminopropyl)-SUPIRO [2, 4, 8, and 10-tetrapod] [5, 5] undecane, etc. are mentioned. These are independent or are used combining two or more kinds. As for the ratio of an aromatic diamine and an aliphatic diamine, it is desirable to use from a heat-resistant point at 20 or less % of the weight to the total quantity of an aromatic diamine / aliphatic diamine.

[0027] As the aforementioned multiple-valued carboxylic acid, for example Oxalic acid, a malonic acid, a succinic acid, A glutaric acid, an adipic acid, a pimelic acid, an azelaic acid, a sebacic acid,

ARUKIRENTE-Tell joint content dicarboxylic acids, such as dodecane 2 acid and eicosane 2 acid, Aliphatic dicarboxylic acids, such as an alkylene carbonate joint content dicarboxylic acid and a butadiene joint content dicarboxylic acid, Aromatic dicarboxylic acids, such as a phthalic acid, an isophthalic acid, a terephthalic acid, and a naphthalene dicarboxylic acid, Butane - 1, 2, 4-tricarboxylic acid, naphthalene - 1, 2, 4-tricarboxylic acid, Tricarboxylic acids, such as trimellitic acid, butane - 1, 2, 3, 4-tetracarboxylic acid, Pyromellitic acid, benzophenone -3, 3', 4, and 4'-tetracarboxylic acid, Tricarboxylic acids, such as diphenyl-ether -3, 3', 4, and 4'-tetracarboxylic acid, Biphenyl -3, 3', 4, and 4'-tetracarboxylic acid, naphthalene [- Carboxylic acids, such as 1, 2 5, and 8-tetracarboxylic acid, an anhydrous TORIMETTO acid etc. are mentioned.] - 2, 3, 6, 7-tetracarboxylic acid, naphthalene - 1, 2, 4, 5-tetracarboxylic acid, naphthalene As for an aliphatic dicarboxylic acid, it is desirable to use less than [20 mol %] in a multiple-valued carboxylic acid from a heat-resistant point. These are independent or are used combining two or more kinds.

[0028] As the aforementioned aromatic diisocyanate, for example 4 and 4'-diphenylmethane diisocyanate (It abbreviates to MDI hereafter), 2, 4-tolylene diisocyanate, 2, 6-tolylene diisocyanate, 1, 5-naphthalene diisocyanate, tolidine di-isocyanate, p-phenyl diisocyanate, 4-4'-diphenyletherdiisocyanate, Aromatic diisocyanate, such as m-xylylene diisocyanate and m-tetramethyl xylylene diisocyanate, 1, 6-hexamethylene di-isocyanate, 2 and 2, 4-trimethylhexamethylene JIISHI cyanate, Cycloaliphatic diisocyanate, such as aliphatic diisocyanate [such as 2, 4, and 4-trimethylhexamethylene JIISHI cyanate,], isophorone diisocyanate, 4, and 4'-dicyclohexylmethane diisocyanate, etc. is mentioned. As for aliphatic diisocyanate, it is desirable to use less than [10 mol %] from a heat-resistant point. These are independent or are used combining two or more kinds.

[0029] The siloxane denaturation polyamidoimide resin of the (A) component used by this invention For example, mixture ((I)/(II) = 0.1/99.9 - 99.9 / 0.1 mole ratios) and trimellitic anhydride of an aromatic diamine or an aliphatic diamine (I), and a siloxane diamine (II) The number of sum total mols of ((I) + (II)) and the mole ratio of TMA (it abbreviates to TMA hereafter) by 1 / 2.20 - 1/2.05 under existence of a non-proton nature polar solvent Make it react at about 50-90 degrees C for about 0.2 to 1.5 hours, and the aromatic hydrocarbon in which water and azeotropy are still more possible is supplied by about 0.1 - 0.5% of the weight of the non-proton nature polar solvent. React at 120-180 degrees C, and the mixture containing siloxane diimide dicarboxylic acid is manufactured. This and aromatic diisocyanate (III) can be manufactured at reacting at about 150-250 degrees C for about 0.5 to 3 hours ((III) = 1/1.50 - 1 / 1.05 mole ratios) ((I) + (II)). Moreover, after manufacturing aromatic diimide dicarboxylic acid, an aromatic hydrocarbon can be removed from the solution by making the solution into about 150-250 degrees C, and it can also manufacture by performing the reaction of this and aromatic diisocyanate. Moreover, as for a siloxane denaturation polyamidoimide resin, it is desirable that it is a varnish containing a non-proton nature polar solvent.

[0030] It is desirable that they are a siloxane diamine and TMA, and the organic solvent that does not react as the aforementioned non-proton nature polar solvent, for example, in order to mention a dimethylacetamide, a dimethylformamide, dimethyl sulfoxide, a N-methyl-2-pyrrolidone, gamma-butyrolactone, a sulfolane, a cyclohexanone, etc. and for an imide-ized reaction to take an elevated temperature, especially a N-methyl-2-pyrrolidone with the high boiling point is desirable. Since a reaction does not fully advance but the moisture content contained in the above-mentioned non-proton nature polar solvent causes [of a polymer] a molecular weight fall by the trimellitic acid which TMA hydrates and generates, it is desirable to be managed at 0.2 or less % of the weight. Moreover, although not restricted, that the solubility of TMA falls and it becomes impossible to perform sufficient reaction when there are many rates of a weight with which a siloxane diamine and TMA were doubled, and since it is conversely disadvantageous as a low and a industrial manufacturing method, a bird clapper is desirable [especially the non-proton nature polar solvent used by this invention] in 10 - 70% of the weight of the range. These are independent or are used combining two or more kinds.

[0031] As for the weight average molecular weight of (A) siloxane denaturation polyamidoimide resin of this invention, it is desirable that it is 30,000-100,000 from the balance of a property, and it is more desirable that it is 45,000-85,000. When there is an inclination for thermal resistance to fall

[this weight average molecular weight] less than by 30,000 and 100,000 is exceeded, there is an inclination for an adhesive property to fall. In this invention, weight average molecular weight is measured using the calibration curve by standard polystyrene by the gel permeation chromatography method (GPC).

[0032] The non-aqueous-solvent system binder constituent of this invention can be made to contain (B) thermosetting resin if needed. As the above-mentioned thermosetting resin, an epoxy resin, phenol resin, polyester resin, polyimide resin, a bismaleimide triazine resin, etc. are mentioned, for example.

[0033] Especially the epoxy resin from the point of an adhesive property and handling nature is desirable. as the above-mentioned epoxy resin For example, the bisphenol A type epoxy resin, a bisphenol female mold epoxy resin, A bisphenol S type epoxy resin, a phenol novolak type epoxy resin, A cresol novolak type epoxy resin, a naphthalene type epoxy resin, and its denaturation object, BIKISHIRE nil diglycidyl ether, YDC1312 (Tohto Kasei make), TMH574 (Sumitomo Chemical make), Epicoat 1031S (product made from oil-ized shell), Aromatic system epoxy resins, such as EPOTOTO 8125 (tradename by Tohto Kasei Co., Ltd.), Neopentyl glycol diglycidyl ether, polypropylene glycol diglycidyl ether, Heterocycle formula epoxy compounds, such as aliphatic system epoxy resins, such as tetrahydrophthalic acid diglycidyl ester, and a triglycidyl isocyanate, EPOLEAD PB3600 (tradename made from Die Cell Chemistry), etc. are mentioned.

[0034] In these, it is desirable to use the epoxy resin which has two or more glycidyl groups, and its hardening accelerator. Moreover, a glycidyl group is so good that there are, and if it is three or more pieces, it is still more desirable. [many] Loadings change with number of glycidyl groups, and the loadings to a silicone denaturation polyamidoimide resin are so good that there are many glycidyl groups at least. Moreover, it is still more desirable if the curing agent of an epoxy resin is used together. These are independent or are used combining two or more kinds.

[0035] As for the loadings of the epoxy resin used by this invention, it is desirable that it is the 5 - 100 weight section to an adhesive property, flexibility, and a heat-resistant point to the (A) component 100 weight section, and it is more desirable that it is 10 - 50 weight section. When there is an inclination for electrolytic-solution-proof nature with these loadings sufficient in under 5 weight sections not to be obtained and the 100 weight sections are exceeded, there is an inclination for a sufficient adhesive property and sufficient flexibility not to be obtained.

[0036] As the curing agent or hardening accelerator of the aforementioned epoxy resin, in an epoxy resin, the thing which reacts, or hardening, if it is a promotion ***** thing, what thing may be used, for example, amines, imidazole derivatives, polyfunctional phenols, and acid anhydrides will be mentioned. As the above-mentioned amines, a dicyandiamide, a diamino diphenylmethane, a guanylurea, etc. are mentioned, for example. As the above-mentioned imidazole derivatives, alkyl group substitution imidazoles, such as a 2-ethyl-4-methyl imidazole, a benzimidazole, etc. are mentioned, for example. As the above-mentioned polyfunctional phenols, novolak phenol type phenol resin, resol type phenol resin, etc. which are a hydroquinone, a resorcinol, bisphenol A and these halogenated compounds, and the addition condensation object of the aforementioned polyfunctional phenols and formaldehyde are mentioned, for example. As the above-mentioned acid anhydrides, phthalic anhydride, a benzophenone tetracarboxylic acid dihydrate, methyl himic acid, etc. are mentioned, for example. Among these, as a hardening accelerator, especially the thing for which imidazole derivatives are used is desirable.

[0037] In the case of amines, the initial complement of these curing agents or a hardening accelerator has the desirable amount to which the equivalent of the active hydrogen of an amine and the weight per epoxy equivalent of an epoxy resin become almost equal. In the case of an imidazole, it does not become equivalent ratio with active hydrogen simply, but it is [0.1 - 10.0 weight section] experientially necessary to the epoxy resin 100 weight section. In the case of polyfunctional phenols, 0.6 to 1.2 hydroxyl equivalent is required to 1Eq of epoxy groups of an epoxy resin. Since a non-hardened epoxy resin remains if there are few amounts of these curing agents or a hardening accelerator, an adhesive property falls, and since an unreacted curing agent and an unreacted hardening accelerator remain if many [too], electrolytic-solution-proof nature falls. These are independent or are used combining two or more kinds.

[0038] In this invention, a non-aqueous solvent is made to dissolve or distribute these constituents so that a solid content may become about 10 - 30% of the weight, and it considers as a non-aqueous-solvent system binder constituent. As the above-mentioned non-aqueous solvent, if solubility is acquired, what thing may be used and a dimethylacetamide, a dimethylformamide, dimethyl sulfoxide, a N-methyl-2-pyrrolidone, gamma-butyrolactone, a sulfolane, a cyclohexanone, etc. will be mentioned, for example. These are independent or are used combining two or more kinds.

[0039] The non-aqueous-solvent system binder constituent and active material of this invention can be mixed, it can apply to an electrode base front face, and an electrode can be manufactured by removing a polar non-aqueous solvent. As the above-mentioned electrode base, aluminum, copper, etc. are mentioned, for example.

[0040] Although a well-known thing can be used as the above-mentioned active material, for example, the end of a carbon powder, such as an amorphous carbon and an artificial graphite, etc. is mentioned, it is desirable that it is the transition-metals oxide which can insert or emit a lithium ion in reversible, and lithium manganese multiple oxides, such as lithium nickel multiple oxides, such as lithium cobalt multiple oxides, such as a cobalt acid lithium, and a nickel acid lithium, and a manganic acid lithium, such mixture, etc. are mentioned as these examples, for example.

[0041] In the above-mentioned lithium nickel multiple oxide, the lithium nickel multiple oxide which replaced the nickel site or the lithium site with at least one or more sorts of metals chosen from aluminum, V, Cr, Fe, Co, Sr, Mo, W, Mn, B, Mg, etc. is sufficient. Also in the above-mentioned lithium manganese multiple oxide, the lithium manganese multiple oxide which replaced the manganese site or the lithium site with at least one or more sorts of metals chosen from Li, aluminum, V, Cr, Fe, Co, nickel, Mo, W, Zn, B, and Mg is sufficient.

[0042] As for the above-mentioned lithium manganese multiple oxide, it is desirable that it is $\text{Li}_x\text{Mn}_y\text{O}_2$. As for Above x, it is desirable that it is the range of $0.2 \leq x \leq 2.5$, and it is [Above y] desirable that it is $0.8 \leq y \leq 1.25$. The amount of Mn eluted from a positive active material since a non-aqueous-solvent system binder constituent exists so that a part of particle front face of a lithium manganese multiple oxide may be worn when manufacturing a non-aqueous-solvent system rechargeable battery, using the above-mentioned lithium manganese multiple oxide as a positive active material can be reduced, the electronic-conduction nature of a positive electrode is secured, and since degradation of the negative electrode by Mn eluted in one side can also be suppressed, the organic electrolytic-solution rechargeable battery which has improved the cell capacity fall by the charge-and-discharge cycle can obtain.

[0043] Although especially a limit does not have a non-aqueous-solvent system rechargeable battery using the above-mentioned electrode For example, it winds through the separator which consists of a polyethylene fine porous membrane etc. Produce a spiral-like winding group, insert this winding group in a cell can, and the nickel tab terminal beforehand welded to the copper foil of a negative-electrode charge collector is welded to a battery can bottome. The electrolytic solution is put into the obtained cell container, and the aluminum tab terminal beforehand welded to the aluminum foil of a positive-electrode charge collector is welded to a lid, and a lid can be arranged in the upper part of a cell can through an insulating gasket, and it can carry out sealing etc. and can manufacture.

[0044] As the above-mentioned electrolytic solution, for example, organic solvents, such as carbonate, ester, ether, ketones, lactone, nitril, amines, amides, sulfur compounds, chlorinated hydrocarbons, and sulfolane system compounds, are mentioned, and independent or two or more kinds of mixed solvents, such as propylene carbonate, ethylene carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, diethyl carbonate, gamma-butyrolactone, a tetrahydrofuran, diethylether, a sulfolane, an acetonitrile, dimethyl carbonate, and a N-methyl-2-pyrrolidone, are desirable As the above-mentioned electrolyte, LiClO_4 , LiPF_6 , LiPF_4 , LiBF_4 , LiCl , LiBr , $\text{CH}_3\text{SO}_3\text{Li}$, and LiAsF_6 grade are mentioned, for example.

[0045] The electrode of this invention is excellent in the adhesion of the binder layer containing an active material, and the metallic foil which is an electrode base, excellent in electrolytic-solution-proof nature and thermal resistance, and even if used under an elevated temperature, it can maintain an electrode base, a binder layer, and the adhesion intensity between binder layers for a long period of time. if an electrode base, a binder layer, and the adhesion intensity between binder layers improve --

a mixture -- the addition of an inner non-aqueous-solvent system binder constituent can be reduced, it is possible to, increase the amount of active materials as a result, and the cell using this electrode can increase a volume energy density. Since the cell using the electrode which maintained an electrode base, a binder layer, and the adhesion intensity between binder layers for a long period of time can maintain an electrode base, a binder layer, and the electric conduction network between binder layers and can perform a charge reaction and an electric discharge reaction uniformly even if it repeats charge and discharge, its cycle-life property can also improve.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE

[Example] Hereafter, this invention is explained in detail based on an example. In addition, unless it refuses especially among an example, the section and % show weight section and weight %, respectively.

[0047] (Composition of a siloxane conversion polyamidoimide resin) with [which connected the reflux condenser] a cock -- the 1l. separable flask equipped with the 25ml moisture fixed quantity receiver, the thermometer, and the stirrer -- as an aroma diamine as 2 and 2-screw [4-(4-amino phenoxy) phenyl] propane and a siloxane diamine -- reactant silicone-oil X-22-161- it taught with the compounding ratio which showed NMP (N-methyl-2-pyrrolidone) in Table 1, respectively as AS (the tradename by Shin-Etsu Chemical Co., Ltd., amine equivalent 416), TMA (trimellitic anhydride), and a non-proton nature polar solvent, and agitated for 30 minutes at 80 degrees C And after supplying 100ml of toluene as an aromatic hydrocarbon in which water and azeotropy are possible, temperature was raised and it was made to flow back at 160 degrees C for 2 hours. It checked that 3.6ml or more of water has collected on a moisture fixed quantity receiver, and that the outflow of water was no longer seen, and removing an effluent collected on the moisture fixed quantity receiver, temperature was raised to about 190 degrees C, and toluene was removed. Then, the solution was returned to the room temperature, the amount which showed MDI (4 and 4'-diphenylmethane diisocyanate) in Table 1 as aromatic diisocyanate was supplied, and it was made to react at 190 degrees C for 2 hours. The NMP solution of the siloxane conversion polyamidoimide resin A-1 and the siloxane conversion polyamidoimide resin A-2 was obtained after the reaction end.

[0048]

[Table 1]

表 1

試 料 名		A-1	A-2
配 合 (部)	BAPP ⁻¹	28.7	32.8
	X-22-161AS ⁻²	58.3	16.6
	TMA ⁻³	56.5	40.4
	NMP ⁻⁴	383.6	307.3
	MDI ⁻⁵	42.0	30.0
加 熱 残 分 (%)		32	26
重 量 平 均 分 子 量		63500	66000

- *1: 2, 2-ビス [4- (4-アミノフェノキシ) フェニル] プロパン
 *2: 反応性シリコンオイル (信越化学工業株式会社製商品名)、
 シロキサン系両末端アミン
 *3: 無水トリメリット酸
 *4: N-メチル-2-ピロリドン
 *5: 4, 4'-ジフェニルメタンジイソシアネート

[0049] (Production of a non-aqueous-solvent system binder constituent)

The material shown in Table 2 to examples 1-6, the siloxane conversion polyamidoimide resin A-1 obtained example of comparison 1, and the siloxane conversion polyamidoimide resin A-2 was added, and the constituent for binders was obtained. After applying the N-methyl-2-pyrrolidone solution (the product made from the Kureha chemistry, tradename KF-1100) of a polyvinylidene

fluoride to rolling copper foil as obtained resin constituent I-VI for binders, and an example 1 of comparison so that it may become about 30 micrometers of dryness thickness, it dried at 120 degrees C for 3 hours, and dryness hardening was carried out at 180 degrees C for 2 hours, and the hardening paint film was obtained. Subsequently, the hardening paint film was stuck on the glass plate which stuck the double-sided tape beforehand, and the rolling copper foil adhesion hardening paint film stuck on the glass plate was obtained. The adhesive property (Peel intensity to rolling copper foil) of this hardening paint film was measured. The result was shown in Table 2.

[0050]

[Table 2]

		表 2						(重量部)
試 料 名		実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	比較例1
		非水溶媒系バインダ組成物						比較樹脂
		I	II	III	IV	V	VI	
(A) 成 分	シロキサン変性アミドイミド樹脂A-1 (固形分32%)	313	313	313	313	313	—	—
	シロキサン変性アミドイミド樹脂A-2 (固形分26%)	—	—	—	—	—	385	—
	ポリフッ化ピリデン樹脂(固形分12%)	—	—	—	—	—	—	833 (固形分100)
(B) 成 分	ビスフェノールA型エポキシ :エポトート8125 *6	40	50	60	50	50	50	—
	エポキシ化ポリブタジエン :エポリードPB3600 *7	10	10	10	5	15	10	—
	2-エチル-4-メチルイミダゾール	0.2	0.2	0.2	0.2	0.2	0.2	—
接 着 性		ピール強度 (KN/m)						
		1	0.9	0.8	0.9	1.1	0.9	0.5

*6: 東都化成株式会社商品名

*7: ダイセル化学株式会社商品名

[0051] (Production of a negative-electrode electrode)

The amorphous carbon of 20 micrometers of example 7 mean particle diameters and the non-aqueous-solvent system binder constituent I are mixed at a rate of 96:4, injection mixture is carried out at a N-methyl-2-pyrrolidone, and a slurry-like solution is produced. This solution is applied to both sides of copper foil with a thickness of 10 micrometers, and it dries to them. a mixture -- a coverage is one side 65 g/m² a mixture -- bulk density becomes 1.0 g/cm³ -- as -- a roll-press machine -- rolling out -- 56mm width of face -- cutting -- a short **-like negative electrode -- a mixture -- the electrode sheet was produced a negative electrode -- a mixture -- the current collection tab of the product [edge / of an electrode sheet] made from nickel -- ultrasonic welding -- carrying out -- a bridge formation of removal of the remains solvent in after that and an electrode, and the water of adsorption, and a non-aqueous-solvent system binder constituent sake -- 180 degrees C -- a 1-hour vacuum drying -- carrying out -- a negative electrode -- a mixture -- the electrode was obtained

[0052] The negative-electrode electrode was obtained like the example 7 except using non-aqueous-solvent system binder constituent II-VI at the time of production of the solution of the shape of an example 8 - 12 slurries.

[0053] The non-aqueous-solvent system binder constituent I is mixed with the artificial graphite of 20 micrometers of example 13 mean particle diameters at a rate of 95:5, injection mixture is carried out at a N-methyl-2-pyrrolidone, and a slurry-like solution is produced. This solution is applied to both sides of copper foil with a thickness of 10 micrometers, and it dries to them. a mixture -- a coverage is one side 65 g/m² a mixture -- bulk density becomes 1.0 g/cm³ -- as -- a roll-press machine -- rolling out -- 56mm width of face -- cutting -- a short **-like negative electrode -- a mixture -- the

electrode sheet was produced a negative electrode -- a mixture -- the current collection tab of the product [edge / of an electrode sheet] made from nickel -- ultrasonic welding -- carrying out -- the bridge formation of removal and the resin constituent for non-aqueous-solvent system binders by the remains solvent in after that and an electrode, and adsorption sake -- 180 degrees C -- a 1-hour vacuum drying -- carrying out -- a negative electrode -- a mixture -- the electrode was obtained [0054] The negative-electrode electrode was obtained like the example 13 except using non-aqueous-solvent system binder constituent II-VI at the time of production of the solution of the shape of an example 14 - 18 slurries.

[0055] Example of comparison 2 negative electrode mixes the amorphous carbon of 20 micrometers of mean particle diameters, and a polyvinylidene-fluoride resin at a rate of 90:10, carries out injection mixture at a N-methyl-2-pyrrolidone, and produces a slurry-like solution. This solution is applied to both sides of copper foil with a thickness of 10 micrometers, and it dries to them. a mixture -- a coverage is one side 65 g/m² a mixture -- bulk density becomes 1.0 g/cm³ -- as -- a roll-press machine -- rolling out -- 56mm width of face -- cutting -- a short **-like negative electrode -- a mixture -- the electrode sheet was produced a negative electrode -- a mixture -- the current collection tab of the product [edge / of an electrode sheet] made from nickel -- ultrasonic welding -- carrying out -- a heat curing of the remains solvent in after that and an electrode, or a removal of the water of adsorption and a binder resin sake -- 160 degrees C -- a 3-hour vacuum drying -- carrying out -- a negative electrode -- a mixture -- the electrode was obtained

[0056] The negative-electrode electrode was obtained like the example 13 except using a polyvinylidene-fluoride resin instead of an example of comparison 3 non-aqueous-solvent system binder constituent.

[0057] About the obtained electrode, electrolytic-solution-proof nature (existence of the abnormalities in appearance in one 1000 times the scale factor of this according to the electron microscope after being 24-hour immersed at 50 degrees C to these using the mixed liquor of the ethylene carbonate / dimethyl carbonate = 1/2 (volume ratio) in which LiPF₆ was dissolved as the electrolytic solution so that a N-methyl-2-pyrrolidone or concentration might be set to 1M) was evaluated. These results were shown in Table 3.

[0058]

[Table 3]

表 3

	使用した非水溶媒系バインダ組成物	電解液 A *8	電解液 B *9
実施例 7	非水溶媒系バインダ組成物 I	外観異常なし	外観異常なし
実施例 8	非水溶媒系バインダ組成物 II	外観異常なし	外観異常なし
実施例 9	非水溶媒系バインダ組成物 III	外観異常なし	外観異常なし
実施例 10	非水溶媒系バインダ組成物 IV	外観異常なし	外観異常なし
実施例 11	非水溶媒系バインダ組成物 V	外観異常なし	外観異常なし
実施例 12	非水溶媒系バインダ組成物 VI	外観異常なし	外観異常なし
実施例 13	非水溶媒系バインダ組成物 I	外観異常なし	外観異常なし
実施例 14	非水溶媒系バインダ組成物 II	外観異常なし	外観異常なし
実施例 15	非水溶媒系バインダ組成物 III	外観異常なし	外観異常なし
実施例 16	非水溶媒系バインダ組成物 IV	外観異常なし	外観異常なし
実施例 17	非水溶媒系バインダ組成物 V	外観異常なし	外観異常なし
実施例 18	非水溶媒系バインダ組成物 VI	外観異常なし	外観異常なし
比較例 2	ポリフッ化ビニリデンのN-メチル-2-ピロリドン溶液 (呉羽化学製、商品名KF-1100)	表面膨潤	表面膨潤
比較例 3	ポリフッ化ビニリデンのN-メチル-2-ピロリドン溶液 (呉羽化学製、商品名KF-1101)	表面膨潤	表面膨潤

*8: 電解液A (濃度が1モル/リットルとなるようにLiPF₆を溶解させたプロピレンカーボネートの混合液)

*9: 電解液B (濃度が1モル/リットルとなるようにLiPF₆を溶解させたエチレンカーボネート/ジメチルカーボネート=1/2 (体積比)の混合液)

[0059] the obtained negative electrode -- a mixture -- the charge and discharge test made to discharge

until it results in neglect final-voltage 1V in discharge current 0.28 mA/cm², after carrying out constant-potential charge of the charge capacity, service capacity, and irreversible capacity of the first time by the single electrode of an electrode by discharge current 0.28 mA/cm² and 5mV. of discharge voltage was performed, and the cycle property was measured by repeating this The result was shown in Table 4 and 5.

[0060]

[Table 4]

表 4

	初 回		
	充電容量 (mAh/g)	放電容量 (mAh/g)	不可逆容量 (mAh/g)
実施例 7	384	351	33
実施例 8	387	354	33
実施例 9	385	353	32
実施例 10	386	354	32
実施例 11	383	349	34
実施例 12	380	345	35
実施例 13	401	368	33

[0061]

[Table 5]

表 5

	初 回		
	充電容量 (mAh/g)	放電容量 (mAh/g)	不可逆容量 (mAh/g)
実施例 14	405	370	35
実施例 15	405	370	35
実施例 16	400	367	33
実施例 17	403	369	34
実施例 18	395	360	35
比較例 2	360	295	65
比較例 3	370	300	70

[0062] (Production of a lithium secondary battery)

the scale-like natural graphite whose mean particle diameter is 1 micrometer as example 19 positive active material considering LiCoO₂ as 89 % of the weight and an electric conduction agent -- 8 % of the weight and a binder -- carrying out -- the non-aqueous-solvent system binder resin constituent I -- 3 % of the weight -- adding -- this -- a N-methyl-2-pyrrolidone -- adding -- mixing -- a positive electrode -- the slurry of a mixture was adjusted the same -- as the negative-electrode matter -- as 95 % of the weight of amorphous carbons of 12 micrometers of mean particle diameters, and a binder -- the non-aqueous-solvent system binder resin constituent I -- 5 % of the weight -- adding -- this -- a N-methyl-2-pyrrolidone -- adding -- mixing -- a negative electrode -- the slurry of a mixture was obtained next, a positive electrode -- thickness applied the slurry of a mixture to both sides of the aluminum foil which is 25 micrometers, and carried out the vacuum drying at 120 degrees C after that for 1 hour. After the vacuum drying, pressing of the electrode was carried out with the roller press, and thickness was set to 190 micrometers. The positive-electrode binder coverage per unit area was 49 mg/cm², and width of face started it by 40mm in the size whose length is 285mm, and it produced the positive electrode. however, a portion with a length [of the ends of a positive electrode] of 10mm -- a positive electrode -- a mixture was not applied, but the aluminum foil was exposed, and the positive-electrode tab was stuck to one of these by pressure by ultrasonic jointing

[0063] on the other hand -- a negative electrode -- thickness applied the slurry of a mixture to both

sides of the copper foil which is 10 micrometers, and carried out the vacuum drying at 120 degrees C after that for 1 hour. After the vacuum drying, pressing of the electrode was carried out with the roller press, and thickness was set to 175 micrometers. The positive-electrode binder coverage per unit area was 20 mg/cm², and width of face started it by 40mm in the size whose length is 290mm, and it produced the negative electrode. this -- a positive electrode -- the same -- a portion with a length [of the ends of a negative electrode] of 10mm -- a negative electrode -- a mixture was not applied, but copper foil was exposed, and the negative-electrode tab was stuck to one of these by pressure by ultrasonic jointing. As for separator, thickness used the micropore film made from polyethylene whose width of face is 44mm by 25 micrometers.

[0064] Subsequently, it piled up in order of a positive electrode, separator, a negative electrode, and separator, this was wound, and it considered as the electrode group. This was inserted in the cell can of single 3 sizes, can bottom welding of the negative-electrode tab was carried out, and the converging section for closing a positive-electrode lid was formed. After pouring into a cell can the electrolytic solution which dissolved one mol /of 6 fluoride [phosphoric-acid] lithiums in the mixed solvent of the ethylene carbonate and diethyl carbonate of 1:1 l. by the volume ratio after this, the positive-electrode tab was welded to the positive-electrode lid, and the caulking lithium secondary battery was obtained for the positive-electrode lid after that.

[0065] The charge-and-discharge cycle property was evaluated using the obtained lithium secondary battery. Charge of the produced lithium secondary battery was charged with constant-voltage current until current was set to 30mA by cell-voltage 4.2V, after charging by the constant current to cell-voltage 4.2V with 300mA of current. Electric discharge performed constant-current discharge until it was set to cell-voltage 2.8V with 300mA of current. This charge-and-discharge cycle was repeated 300 times. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0066] Except using resin II-IV for binders for the binder of 20 to example 24 positive electrode, and a negative electrode, the lithium secondary battery was produced like the example 19, and the charge-and-discharge cycle property was evaluated like the example 19. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0067] Except using the artificial graphite of 20 microns of mean particle diameters for an example 25 negative-electrode active material, the lithium secondary battery was produced like the example 19, and the charge-and-discharge cycle property was evaluated like the example 19. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0068] Except using resin II-IV for binders for the binder of 26 to example 30 positive electrode, and a negative electrode, the lithium secondary battery was produced like the example 25, and the charge-and-discharge cycle property was evaluated like the example 25. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0069] Except using a polyvinylidene-fluoride resin for the binder of example of comparison 4 positive electrode, and using a polyvinylidene fluoride for the binder of a negative electrode 10% of the weight 5% of the weight, the lithium secondary battery was produced like the example 19, and the charge-and-discharge cycle property was evaluated like the example 19. The service-capacity maintenance factor of the service-capacity 100 cycle eye of 1 cycle eye and a 300 cycle eye is shown in Table 6.

[0070] Except using a polyvinylidene fluoride for the binder of example of comparison 5 positive electrode, and using a polyvinylidene fluoride for the binder of a negative electrode 10% of the weight 5% of the weight, the lithium secondary battery was produced like the example 25, and the charge-and-discharge cycle property was evaluated like the example 25. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0071]

[Table 6]

表 6

試料名	正極活物質	負極活物質	正・負極結着剤	1サイクル目 放電容量 (mAh)	100サイクル目放電 容量維持率 (%)	300サイクル目放電 容量維持率 (%)
実施例19	LiCoO_2	非晶質炭素	非水溶媒系パイ ンダ組成物 I	532	93	89
実施例20	LiCoO_2	非晶質炭素	非水溶媒系パイ ンダ組成物 II	535	93	88
実施例21	LiCoO_2	非晶質炭素	非水溶媒系パイ ンダ組成物 III	536	94	89
実施例22	LiCoO_2	非晶質炭素	非水溶媒系パイ ンダ組成物 IV	538	95	90
実施例23	LiCoO_2	非晶質炭素	非水溶媒系パイ ンダ組成物 V	533	93	89
実施例24	LiCoO_2	非晶質炭素	非水溶媒系パイ ンダ組成物 VI	535	94	90
比較例4	LiCoO_2	非晶質炭素	ポリフッ化ビニ リデン樹脂	420	88	76
実施例25	LiCoO_2	人造黒鉛	非水溶媒系パイ ンダ組成物 I	620	89	83
実施例26	LiCoO_2	人造黒鉛	非水溶媒系パイ ンダ組成物 II	623	88	84
実施例27	LiCoO_2	人造黒鉛	非水溶媒系パイ ンダ組成物 III	625	88	83
実施例28	LiCoO_2	人造黒鉛	非水溶媒系パイ ンダ組成物 IV	630	90	85
実施例29	LiCoO_2	人造黒鉛	非水溶媒系パイ ンダ組成物 V	615	87	82
実施例30	LiCoO_2	人造黒鉛	非水溶媒系パイ ンダ組成物 VI	625	88	84
比較例5	LiCoO_2	人造黒鉛	ポリフッ化ビニ リデン樹脂	510	65	21

[Translation done.]

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